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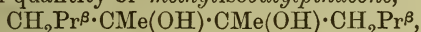






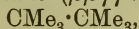
## Organic Chemistry.

*iso*Hexane and a New Dodecane. LATHAM CLARKE and R. NORRIS SHREVE (*Amer. Chem. J.*, 1906, 35, 513—519).—*iso*-Hexane (ethylisobutyl) can be prepared in a yield of 57 per cent. of the theoretical by the reduction of methylisobutylcarbinol. Methylisobutyl ketone, prepared by boiling ethyl isopropylacetoacetate for six hours with 10 per cent. potassium hydroxide, boils at 119° under 765 mm. pressure. Methylisobutylcarbinol can be obtained by mixing an ethereal solution of the ketone with water and gradually adding sodium; a small quantity of *methylisobutylpinacone*,



is produced simultaneously as a viscous, oily liquid which has a fishy odour, boils at 245°, and is soluble in alcohol, ether, ethyl acetate, acetone, benzene, or glacial acetic acid, and insoluble in water. On reducing this pinacone with hydrogen iodide, *methylisobutylcarbinyl iodide*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CHMeI}$ , is obtained as a colourless, oily liquid which boils and partially decomposes at 158—160°, and is soluble in the usual organic solvents, but insoluble in water. The formation of this iodide is attended by the production of a small quantity of a *dodecane* (*dimethyldiisobutylethane*),  $\text{CH}_2\text{Pr}^\beta \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{CH}_2\text{Pr}^\beta$ , which forms a colourless, oily liquid with a faint odour, boils at 208—210°, and is soluble in light petroleum, and slightly so in alcohol. E. G.

Hexamethylethane. LOUIS HENRY (*Compt. rend.*, 1906, 142, 1075—1076).—*Hexamethylethane* ( $\beta\beta\gamma\gamma$ -tetramethylbutane),



is an accessory product in the synthesis of pinacolyl alcohol by the interaction of acetaldehyde and magnesium *tert*-butyl bromide. It crystallises from ether in barbed lamellæ, has a piquant, penetrating odour, melts at 103—104°, and boils at 106—107° under 765 mm. pressure. T. A. H.

Composition of Light Petroleum. LUIGI BALBIANO and VINCENZO PAOLINI (*Gazzetta*, 1906, 36, i, 251—256. Compare Abstr., 1902, ii, 109).—Fourteen kilos. of American petroleum gave 3.5 grams of mercurous acetate when treated with mercuric acetate, whilst acetone and propaldehyde were found in the solution. These may have been formed by oxidation of  $\beta$ -methyl- $\Delta^\beta$ -pentylene.

T. H. P.

New Constituents of Coal Tar. FELIX B. AHRENS (*Chem. Centr.*, 1906, i, 510—511; from *Verh. Ges. Deut. Naturforsch. Aerzte*, 1904, ii, 137—138. Compare Abstr., 1903, i, 515; 1904, i, 615; 1905, i, 232).—In a fraction from the benzene receiver which boiled at 20—30°, butylene and a compound which contained sulphur and resembled carbon disulphide, but was not identical with it, have



been found. Amylene was isolated from a fraction boiling at 30—40°. 2:3-Dimethylpyridine has been obtained from a commercial sample of  $\alpha\beta$ -picoline; it boiled at 162—163° and yielded a picrate which melted at 183° and was almost insoluble in alcohol or water.

E. W. W.

**Decomposition of Bromoform under the Influence of Light and Air.** NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1906, i, 441—442; from *Pharm. Weekblad*, 43, 2—8. Compare this vol., i, 57).—When a current of air is passed through boiling bromoform in sunlight, bromine, hydrogen bromide, and carbon tetrabromide are produced. The primary reactions have already been investigated in the case of chloroform and iodoform. By the action of light in the presence of oxygen, carbon monoxide is oxidised to the dioxide, hydrogen bromide forms water and bromine, and by the action of the latter on bromoform, carbon tetrabromide and hydrogen bromine are obtained.

When bromoform, together with a small quantity of oxygen, is exposed to sunlight in sealed tubes, the action appears to result in the formation of carbon monoxide (1 mol.), bromine (1 mol.), and hydrogen bromide (1 mol.); when a large quantity of oxygen is present, carbon dioxide (2 mols.), water (1 mol.), and bromine (3 mols.) are formed. Carbon oxybromide is an intermediate product. When bromoform is exposed to sunlight in tubes from which the air has been almost completely removed, carbon monoxide and hydrogen bromide are obtained in the proportion of 13·7 to 47 1/10-equivalents; this result is consistent with the hypothesis that the bromoform is decomposed into carbon dibromide and hydrogen bromide, and that the former is decomposed by the water in the wash-bottles, forming carbon monoxide and hydrogen bromide. In addition to these products, 12 1/10-equivalents of bromine are also liberated. The liberation of bromine must be assumed to result from the intermediate formation of some other carbon hydrogen bromine compound, possibly of symmetrical tetrabromoethane,  $\text{CHBr}_2\text{CHBr}_2$ , and the decrease of sp. gr. of the contents of the tube from 2·882 to 2·872 at 19° may be an indication of this change. The presence of carbon tetrabromide could not be detected in this case.

E. W. W.

**Comparison of the Decomposition of Chloroform, Bromoform, and Iodoform under the Influence of Light** NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1906, i, 442; from *Pharm. Weekblad*, 43, 8—10. Compare preceding abstract).—Experiments on the action of light alone on chloroform, bromoform, and iodoform have shown that whilst chloroform is not affected, iodoform is partially decomposed in consequence of the presence of traces of air, and bromoform is decomposed spontaneously, probably forming carbon dibromide and hydrogen bromide. By the action of air in the absence of sunlight at higher temperatures, iodoform becomes violet in a quarter of an hour, and the separation of iodine is distinctly visible in an hour; bromoform becomes acid and slightly yellow

in an hour, and gives a precipitate with silver nitrate, whilst chloroform does not give any reaction with silver nitrate after four hours.

E. W. W.

**Decomposition of Iodoform dissolved in Chloroform by Diffused Daylight and by Radium Rays.** WILLEM P. JORISSEN and WILHELM E. RINGER (*Chem. Centr.*, 1906, i, 442; from *Chem. Weekblad*, 2, 799—802. Compare preceding abstracts).—When a solution of iodoform in chloroform is exposed to diffused sunlight in the presence of oxygen, it appears to be completely decomposed. A solution of iodoform in carbon disulphide covered with water does not show any change for some time, and then decomposes only very slowly. A solution of iodoform in chloroform frozen by means of liquid air is not affected by bright daylight so long as it remains solid.

By the action of 5 mg. of radium bromide on 50 c.c. of a 1 per cent. solution of iodoform in chloroform at 25°, 75·2 per cent. of the iodine was liberated, whilst in a similar solution which was not exposed to the action of radium bromide only 18·8 per cent. of the iodine was found in a free state. The colour of the iodine solution formed by the action of the radium bromide was not so dark as that of similar solutions obtained by the action of daylight.

E. W. W.

**Abnormality in Melting Points of Amides derived from Aliphatic Sulphonic Acids.** MAURICE DUGUET (*Bull. Acad. roy. Belg.*, 1906, 87—120).—*isoPropanesulphonic chloride*,  $\text{CHMe}_2 \cdot \text{SO}_2\text{Cl}$ , prepared from phosphorus pentachloride and the corresponding alkali sulphonate, boils at 79° under 18 mm. pressure. Its solution in ether on treatment with dry ammonia yields the corresponding *sulphonamide*, which crystallises from ether on addition of light petroleum and melts at 60°. *isoPropanesulphonanilide* crystallises from a mixture of alcohol and water in colourless, pearly leaflets and melts at 84°. *isoPropanesulphon- $\alpha$ -naphthylamide* crystallises from a mixture of alcohol and water in slender needles and melts at 134°. *Butanesulphonic chloride* is a mobile, highly-refractive liquid, and boils at 96—97° under 18 mm. pressure. *Butanesulphonamide* crystallises from a mixture of ether and light petroleum in silky leaflets and melts at 45°. The corresponding *anilide* melts between -10° and -15° and the  *$\alpha$ -naphthylamide* in colourless spangles melting at 60·5°.

*Methanesulphon- $\alpha$ -naphthylamide* crystallises in slender, silky needles and melts at 125—126°. *Ethanesulphon- $\alpha$ -naphthylamide* forms long, colourless prisms and melts at 66°. *Propanesulphon- $\alpha$ -naphthylamide* melts at 84°. *isoButanesulphon- $\alpha$ -naphthylamide* crystallises in colourless spangles and melts at 107°. *isoPentanesulphon- $\alpha$ -naphthylamide* forms colourless, pearly spangles and melts at 90—91°.

The melting points of the series of amides, anilides, and  *$\alpha$ -naphthylamides* described in this and the former paper (*Abstr.*, 1902, i, 428) decrease irregularly as each series is ascended; further, whilst the melting-point curve of the amides of the *iso*-acids is below that of the amides of the normal acids, the reverse is true of the curves for the anilides and  *$\alpha$ -naphthylamides* of the *iso*- and *normal* acids. Similar examples of the fall in melting point as the series are ascended are shown

by the aromatic sulphonamides (Abstr., 1900, i, 147) and the halogen and other derivatives of these described by Chattaway (Trans., 1905, 87, 145). Determinations of the molecular weights of the lower members of the series of compounds now described indicate that in dilute solutions they are not polymerised, but it is not certain that their high melting points are not the result of polymerisation in the solid state. It is pointed out also that there is a possibility of tautomerism in these compounds between the forms  $R \cdot SO_2 \cdot NH_2$  and  $R \cdot SO(OH) \cdot NH$ , and that eventually each may be found to exist in two forms having different melting points. Thus, in the case of isopropane-sulphonamide, one specimen prepared from isopropanesulphonic chloride, which had been kept for seven years, melted at  $19-20^\circ$  instead of  $60^\circ$ , but so far it has proved impossible to repeat this experience in the case of this or any other sulphonamide.

T. A. H.

**Influence of Oxidation of Ethyl Alcohol on the Maturing of Brandy and Wine.** AUGUSTE TRILLAT (*Chem. Centr.*, 1906, i, 580—581; from *Bull. Assoc. Chim. Sucr. Dist.*, 1905, 23, 495—503).—In confirmation of the results obtained by previous workers, it is shown that ethyl, propyl, butyl, and amyl alcohols are readily oxidised spontaneously to acetals, especially in the presence of ferric chloride or hydrochloric acid. Having found that acetals give a blue or green coloration with dimethylaniline and dilute sulphuric acid, owing probably to the formation of compounds of the type  $NMe_2 \cdot C_6H_4 \cdot Me \cdot CH \cdot C_6H_4 \cdot NMe_2$ , the author has employed the reaction in detecting acetals in a number of brandies and liqueurs, and suggests that the maturing of spirits and wines is due partly to the formation of these acetals, which are highly aromatic substances, and partly to the formation of esters. It has been shown that *Mycoderma vini* materially increases the amount of aldehyde in wine, with the result that the wine becomes turbid, loses its colour, and in the presence of potassium salts may even acquire a bitter taste.

P. H.

**Constitution of Pinacolin and its Derivatives.** MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1906, 7—41. Compare Abstr., 1896, i, 591, 662; 1902, i, 79).—The solid chloride,  $CMe_3 \cdot CMeCl_2$ , obtained by the action of phosphorus pentachloride on pinacolin, is now shown to be identical with Faworsky's chloride, since both on treatment with alcoholic potash furnish the same unsaturated liquid chloride,  $CMe_3 \cdot CCl : CH_2$ . The existence of an isomeride (boiling point  $93^\circ$ ) of this unsaturated chloride, obtained by the action of alcoholic potash on the by-products of the action of phosphoric chloride on pinacolin, is confirmed. By the action of sodium on the liquid chloride,  $CMe_3 \cdot CCl : CH_2$ ,  $\gamma$ -dimethyl- $\Delta^a$ -butylene is produced together with small quantities of an acetylenic hydrocarbon and a paraffin.

*Primary pinacolyl acetate*,  $CMe_3 \cdot CH_2 \cdot CH_2 \cdot OAc$ , produced by the action of potassium acetate on the crude  $\gamma$ -dimethyl- $\Delta^a$ -butylene hydrobromide, obtained by the addition of hydrogen bromide to the impure hydrocarbon referred to above, is a colourless liquid, possessing an agreeable fruity odour and boiling at  $153-157^\circ$ . When hydrolysed with potassium hydroxide, it furnishes primary pinacolyl alcohol,



$\text{CMe}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , which is colourless and mobile, has a faint aromatic odour, and solidifies between  $-60^\circ$  and  $-65^\circ$ . When treated with hydrogen bromide, the alcohol yields the corresponding *pinacolyl bromide*, and this is converted into pinacolyl acetate by potassium acetate, no isomerisation into the symmetrical isomeride taking place. Similarly, no isomerisation into a symmetrical isomeride is brought about by heating the bromide at  $100^\circ$  with hydrobromic acid or by treatment with alkalis. On oxidation with chromic acid, the alcohol yields a mixture of a new *hexoic acid* [ $\beta\beta$ -dimethylbutyric acid],  $\text{CMe}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  (a colourless liquid boiling at  $185$ — $190^\circ$ ), and the corresponding  $\beta\beta$ -dimethylbutaldehyde,  $\text{CMe}_3 \cdot \text{CH}_2 \cdot \text{CHO}$ , which boils at  $100$ — $112^\circ$ .

The products described in the preceding paragraph are derived in the first instance from the hydrobromide prepared from the crude  $\gamma$ -dimethyl- $\Delta^a$ -butylene. If, however, this hydrocarbon in a pure state is treated with hydrogen bromide, it furnishes an additive product, which on treatment with potassium acetate yields no primary pinacolyl acetate, but only  $\beta\gamma$ -dimethyl- $\Delta^b$ -butylene,  $\text{Me}_2\text{C}:\text{CMe}_2$ , so that under these circumstances symmetrical isomerisation does occur. These results are in harmony with the abnormal cases recorded by Ipatieff and Dechanoff (Abstr., 1904, i, 705), and it may be assumed that the impurities associated with the crude hydrocarbon in this case exert the same action as the acetic acid employed as a solvent by Ipatieff and Dechanoff.

When the Grignard reaction is applied to isopropyl bromide and acetone, the principal product is probably  $\text{CHMe}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ ; this, like pinacolyl alcohol, boils at about  $120^\circ$ , and the corresponding bromide on treatment with alcoholic potash yields  $\beta\gamma$ -dimethyl- $\Delta^b$ -butylene.

When aldehyde is treated with magnesium *tert*.-butyl bromide crotonaldehyde, a crystalline substance, which boils at about  $110^\circ$ , and a *hexyl alcohol*, which may have the constitution  $\text{CMe}_3 \cdot \text{CHMe} \cdot \text{OH}$ , are produced. The hexyl alcohol boils at  $116$ — $125^\circ$ ; the corresponding *hexyl bromide* boils at  $115$ — $125^\circ$ , and when treated with potassium acetate yields  $\beta\gamma$ -dimethyl- $\Delta^b$ -butylene.

The author discusses the "ketone" and "oxide" formulæ assigned to pinacolin in the light of these new results, and points out that neither is capable of giving a full explanation of the reactions of pinacolin and its derivatives, and that probably no single formula is capable of doing this.

T. A. H.

**Synthesis of Pentamethylethanol.** LOUIS HENRY (*Compt. rend.*, 1906, 142, 1023—1024).—When ethyl chloroisobutyrate is treated with magnesium methyl bromide dissolved in ether, the pentamethyl-ethanol,  $\text{CMe}_3 \cdot \text{CMe}_2 \cdot \text{OH}$ , of Butleroff (Abstr., 1875, 1248) is obtained. The chloride melts at  $130^\circ$ .

T. A. H.

**Mode of Formation of Polyhydric Alcohols.** WILLIAM OECHSNER DE CONINCK (*Chem. Centr.*, 1906, i, 130; from *Rev. gén. Chim.*, 1905, 8, 347).—The fermentation process by which glycerol is supposed to be formed in plant cells, namely, the reduction of formaldehyde according to the equation  $3\text{CH}_2\text{O} + \text{H}_2 = \text{C}_3\text{H}_5(\text{OH})_3$ , may in

a similar way give rise to other alcohols. If two atoms of hydrogen react with one, two, three, four, or five molecules of formaldehyde, methyl alcohol, glycol, glycerol, erythritol, or arabitol is formed. Higher members of the series may also be produced in the same manner.

H. M. D.

**Vegetable Lecithins.** ERNST WINTERSTEIN and O. HIESTAND (*Zeit. physiol. Chem.*, 1906, 47, 490—498. Compare Abstr., 1904, ii, 141).—The vegetable lecithins vary in their percentage of phosphorus. They yield on hydrolysis, in addition to choline, fatty acids, and glycerophosphoric acid, a considerable amount of sugar, in some cases as much as 16 per cent. The sugar is a mixture of hexoses and pentoses. It is thus doubtful if the vegetable lecithins are the same as those of animal origin. Whether there is any kephalin also is doubtful. It therefore appears wise to adopt the more general term phosphatides for these substances.

W. D. H.

**Difluorochloroacetic Acid.** FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1906, 42—51).—*Difluorochloroacetic acid*,  $\text{CClF}_2\cdot\text{CO}_2\text{H}$ , is prepared by exposing difluoroacetic acid (Abstr., 1903, i, 727) to the action of dry chlorine in sunlight. The action proceeds slowly, 12 grams of the acid being chlorinated in the course of a month. It fumes on exposure to air, has a strong odour, melts at  $22.9^\circ$ , and boils at  $121.5^\circ$ . In aqueous solution, the maximum electrical conductivity was found to be 392.3 and the coefficient of ionisation 99.66 at a dilution  $N/256$ . Comparison of these constants with those of trichloroacetic and fluorodichloroacetic acids shows that the substitution of chlorine by fluorine intensifies the acid character. The *potassium*, *barium*, and *silver* salts were prepared. The last-mentioned salt is very unstable, and is slowly hydrolysed by water, forming oxalic, hydrochloric, and hydrofluoric acids. The same decomposition of the silver salt takes place more slowly in alcohol, some ethyl difluorochloroacetate being also formed in this case. A similar hydrolysis of the alkali and alkaline-earth salts occurs in presence of excess of sodium hydroxide. This hydrolysis differs in character from that which takes place with other trihaloid acetic acids under similar conditions, these furnishing usually formic acid and a trihaloid methane. The author has observed a similar difference in the behaviour of the group  $\cdot\text{CCl}_2\text{F}$  in toluene derivatives (compare Abstr., 1899, i, 197, and 1900, i, 637).

T. A. H.

**Indian Ghedda-wax** GEORG BUCHNER (*Chem. Zeit.*, 1906, 30, 528—529).—In order to show that Ghedda-wax, obtained from the following species of Indian bees, *Apis indica*, *A. dorsata*, or *A. florea*, is in reality closely related to the ordinary beeswax of *Apis mellifica*, the author has determined the melting point, acid saponification, and iodine numbers of specimens of these various waxes, and the results obtained show that qualitatively they are all the same, any differences in composition being due only to the quantitative distribution of the various constituents.

P. H.



**Stereoisomerism in the Group of Unsaturated  $\alpha\beta$ -Acyclic Acids.** EDMOND E. BLAISE and P. BAGARD (*Compt. rend.*, 1906, 142, 1087—1089).—It has been shown previously (*Abstr.*, 1904, i, 369) that the distillation of  $\alpha$ -hydroxy-acids in which the hydroxyl group is attached to a secondary carbon atom may be utilised for the preparation of aldehydes. This investigation has now been extended to  $\alpha$ -hydroxy-acids in which the hydroxyl group is attached to a tertiary carbon, and it is found that the amount of ketone produced in this distillation decreases as the molecular weight of the acid increases; thus it varies from 48 per cent. in the case of  $\alpha$ -hydroxy- $\alpha$ -methylpropionic acid to 5 per cent. in the case of  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid, and, conversely, the quantity of unsaturated acid simultaneously produced increases. The two acids here mentioned yield lactides, but the production of lactides ceases beyond the  $C_6$  acids of the series.

When the unsaturated acid produced by distillation is capable of existing in two stereoisomeric forms, it is, as a rule, the less stable which preponderates, and this tendency grows as the series is ascended; thus,  $\alpha$ -hydroxy- $\alpha$ -methylpropionic acid furnishes angelic and tiglic acids in about equal proportions, but  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid yields the less stable isomeride almost pure. In cases where a long chain is attached to the alcoholic carbon atom, there may be a migration of the ethylenic linking with the production of some  $\beta\gamma$ -unsaturated acid; this occurs in the distillation of  $\alpha$ -hydroxy- $\alpha$ -propylvaleric acid. The unsaturated acids obtained by this reaction have been isolated and characterised by conversion into their amides by the method used by Bodroux (*Abstr.*, 1904, i, 662).

The difference between the boiling points of two stereoisomeric unsaturated acids or of their esters decreases as the molecular weight increases. The relative stability towards reagents and heat of the less stable isomerides increases with the molecular weight; thus, whilst tiglic and angelic acids furnish the same bromide, the two ethylcrotonic acids yield different bromides. The less stable isomerides are very sensitive to the action of halogen acids, which transform them into the stable isomerides. Similarly, phosphorus trichloride transforms the less stable isomerides quantitatively into chlorides of the stable acids.

It is pointed out that *cis* and *trans* are no longer suitable descriptive prefixes for the two forms of unsaturated stereoisomeric acids, and it is suggested that they be replaced by the terms *labile* and *stable*, which are abbreviated by the author into *lab.* and *st.* T. A. H.

**Ketone-cyanohydrins.** A. J. ULTÉE (*Ber.*, 1906, 39, 1856—1858).—In reference to Bucherer and Grolée's work on this subject (this vol., i, 405), the author calls attention to prior work of his own (this vol., i, 5). C. S.

**Equilibrium in the System, Glucinum Oxide, Oxalic Anhydride, and Water.** CHARLES L. PARSONS and WM. O. ROBINSON (*J. Amer. Chem. Soc.*, 1906, 28, 555—569).—Experiments are described which show that the only definite hydrated oxalates

of glucinum are  $\text{GlC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{GlC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . The oxalate,  $\text{GlC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  (Rosenheim and Woge, Abstr., 1898, ii, 71), forms orthorhombic crystals [ $a:b:c=0.853:1.0:1.645$ ], and is soluble in less than its own weight of water at  $100^\circ$ , and but little less so at the ordinary temperature. The oxalate,  $\text{GlC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , is obtained by heating the trihydrate at  $100\text{--}105^\circ$ .

The acid oxalate described by Rosenheim and Woge (*loc. cit.*) could not be obtained, and the existence of any such salt is considered improbable.

The anhydrous oxalate cannot be obtained, since it is impossible to remove the last trace of water without simultaneously decomposing the oxalate.

An investigation of the so-called basic oxalates of glucinum has shown that these substances are not definite compounds, but consist of solid solutions of the oxalate in the hydroxide. E. G.

**Reaction of Nitrous Anhydride with Ethyl Malonate.** RICHARD S. CURTISS (*Amer. Chem. J.*, 1906, 35, 477—486. Compare Abstr., 1905, i, 507).—When the gases evolved by the action of warm nitric acid on arsenious oxide are passed into ethyl malonate at  $0^\circ$ , a green oil is formed which consists chiefly of ethyl mesoxalate, together with small quantities of ethyl isonitrosomalonate and of oxalic and acetic acids and their esters. By suitable treatment, the green oil can be made to yield either ethyl oxomalonnate, mesoxalic acid, or ethyl mesoxalate.

Ethyl mesoxalate can be thus obtained in a yield of 90 per cent. or more. It is volatile in the air, and distils under 40—50 mm. pressure without undergoing any marked decomposition, except the loss of water with formation of ethyl oxomalonnate. One gram of water at  $22^\circ$  dissolves 1.3 grams; 1 gram of ethyl malonnate dissolves 0.6 gram; and 1 c.c. of benzene at  $22^\circ$  dissolves 0.2 gram of the ester. The ester is also easily soluble in ether, acetone, chloroform, or alcohol.

If ethyl malonnate is only partially saturated with the nitrogen oxides, ethyl isonitrosomalonnate is obtained; its potassium, *silver*, *sodium*, and *ammonium* salts are described. The observation of Baeyer (*Annalen*, 1864, 131, 293) and of Conrad and Bischoff (Abstr., 1880, 629), that hydrogen cyanide is formed by the decomposition of *iso*-nitrosomalonic acid in aqueous solution, could not be confirmed.

If pure crystalline ethyl mesoxalate is heated in a test-tube at its melting point ( $57^\circ$ ), water condenses on the cool part of the tube, and ethyl oxomalonnate remains as a green oil. On cooling the tube and allowing the water to come into contact with the green oil, combination takes place immediately, the green colour disappears, and on touching the colourless liquid with a glass rod, the original crystalline substance is obtained.

Phenylhydrazine reacts with ethyl oxomalonnate with formation of an amber-coloured oil which has acid properties and yields a yellow *potassium* salt. E. G.

**Preparation of the Salts of Formaldehydesulphoxylic Acid.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 165807).—The salts of

formaldehydesulphoxylic acid are obtained when the formaldehyde-bisulphite compounds or the product of the interaction of formaldehyde and a hyposulphite is treated with reducing agents. Dry sodium hyposulphite is dissolved in 40 per cent. aqueous formaldehyde and the solution heated to boiling for ten minutes with zinc dust and acetic acid. The zinc is then precipitated with sodium carbonate and the filtrate evaporated down under diminished pressure until a solid mass is obtained consisting of sodium formaldehydesulphoxylate mixed with a small proportion of sodium acetate. A similar result is produced by reducing the formaldehydebisulphite compound either with acetic acid and iron filings or aluminium powder, or with stannous chloride.

G. T. M.

**Basic Properties of Oxygen. Additive Compounds of the Halogen Acids and Organic Substances containing Oxygen.** DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1906, **28**, 588—590. Compare *Trans.*, 1904, **85**, 919, 1098; 1905, **87**, 784; *Abstr.*, 1905, **i**, 254, 677).—By the action of the halogen hydrides on acetaldehyde, acetic acid, and ethyl acetate at low temperatures, considerable heat is developed, and the following additive compounds are obtained, which are crystalline, melt sharply, and form supersaturated solutions in the liquid halogen hydride used in their preparation.

The compound  $2\text{CH}_3\cdot\text{CHO}, 3\text{HCl}$  melts at  $-18^\circ$ , the compound  $2\text{CH}_3\cdot\text{CO}_2\text{H}, 3\text{HCl}$  at  $-53^\circ$ , and the compound  $\text{CH}_3\cdot\text{CO}_2\text{Et}, 2\text{HCl}$  at  $-75^\circ$ . The methyl alcohol compound,  $3\text{CH}_3\cdot\text{OH}, 2\text{HCl}$ , melts at  $-64^\circ$ .

The compound  $2\text{CH}_3\cdot\text{CHO}, 3\text{HBr}$  melts at  $-15^\circ$ , and the compound  $2\text{CH}_3\cdot\text{CO}_2\text{Et}, 3\text{HBr}$  at  $-40^\circ$ . Acetic acid does not unite with hydrogen bromide or iodide at low temperatures.

The compound  $3\text{CH}_3\cdot\text{CHO}, 2\text{HI}$  melts at  $-32^\circ$ , and the compound  $\text{CH}_3\cdot\text{CO}_2\text{Et}, \text{HI}$  at  $-23^\circ$ .

E. G.

**Decomposition of Chloral Hydrate by Exposure to Light and Air.** NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1906, **i**, 650; from *Pharm. Weekblad*, 1906, **43**, 42—47).—Chloral hydrate, when exposed to tropical sunlight in an exhausted tube, is decomposed according to the following equation:  $\text{CCl}_3\text{CHO}, \text{H}_2\text{O} = 3\text{HCl} + 2\text{CO}$ . When sealed up in tubes containing an insufficient supply of oxygen, a portion of the substance is also decomposed as follows:  $\text{CCl}_3\text{CHO}, \text{H}_2\text{O} + 2\text{O} = 3\text{HCl} + 2\text{CO}_2$ , although it may be that the carbon dioxide is only formed by the subsequent oxidation of the monoxide produced according to the first equation. In the presence of an excess of oxygen, the following decompositions take place:  $\text{CCl}_3\text{CHO}, \text{H}_2\text{O} + 2\text{O} = 3\text{HCl} + 2\text{CO}_2$  and  $2\text{CCl}_3\text{CHO}, \text{H}_2\text{O} + 7\text{O} = 3\text{H}_2\text{O} + 6\text{Cl} + 4\text{CO}_2$ .

P. H.

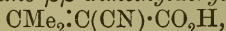
**A Soluble Polychloral.** SIMON GÄRTNER (D.R.-P. 165984).—By treating chloral with pyridine or other amines in the cold and then acidifying the product, a stable, homogeneous polymeride of chloral is obtained, which retains the soporific action of the simple aldehydehydrate, but is less poisonous, and differs from the polychlorals previously described in dissolving in water or alcohol, slowly at the



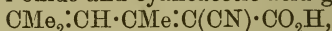
ordinary temperature and rapidly on boiling, to yield, respectively chloral hydrate or chloral alcoholate.

If trimethylamine is employed to induce this polymerisation, it should be used in dilute solutions of inert solvents, otherwise the reaction is very violent and an ill-defined heterogeneous product is obtained.  
G. T. M.

**Condensation of Ketones with Cyanoacetic and Malonic Acids.** EMIL KNOEVENAGEL (D.R.-P. 162281. Compare Abstr., 1905, i, 169; also Komppa, Abstr., 1901, i, 114).—Acetone condenses with cyanoacetic acid in presence of piperidine hydrochloride on the water-bath, forming *α*-cyano-ββ-dimethylacrylic acid,



melting at 130°. Acetophenone and cyanoacetic acid give *α*-cyano-β-phenyl-β-methylacrylic acid,  $\text{CPhMe:C(CN)\cdot CO}_2\text{H}$ , melting at 135—136°. Mesityl oxide and cyanoacetic acid give the acid,



melting at 96°. When acetone and cyanoacetic acid are heated for a long time with ethylamine, carbon dioxide is evolved, and *α*-dicyano-ββ-dimethylbutyric acid,  $\text{CN\cdot CH}_2\text{:CMe}_2\text{:CH(CN)\cdot CO}_2\text{H}$ , melting at 196—197°, is formed. Acetone and malonic acid yield ββ-dimethylacrylic acid.  
C. H. D.

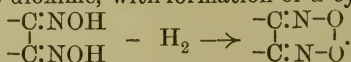
*See errata, V. 90<sup>22</sup> p. 1265*

**Behaviour of Acetoxime and of Dioximes towards Sodium Hypochlorite.** ~~The~~ **Properties of Carbon Tetrabromide.** GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1906, 41, 415—426).—The action of sodium hypochlorite on acetoxime yields, not acetoxime hypochlorite, as was stated to be the case by Möhlau and Hofmann (Abstr., 1887, 795), but firstly β-chloro-β-nitrosopropane, which afterwards undergoes oxidation to β-chloro-β-nitropropane. β-Chloro-β-nitrosopropane,



has a pungent odour and the characteristic blue colour of nitrolic liquid compounds, and under 18 mm. pressure boils at about 7° giving a colourless vapour, whilst under the ordinary pressure it boils and decomposes at about 68°.

With sodium hypochlorite, *p*-quinonedioxime gives *p*-dinitrobenzene and β-naphthaquinonedioxime yields 1 : 2-dinitrosonaphthalene, whilst the dioximes of benzyl and of camphoquinone are transformed into the corresponding peroxides. The reaction between sodium hypochlorite and the dioximes may be regarded as the elimination of two atoms of hydrogen from the dioxime, with formation of a cyclic compound :



The mode of action of sodium hypochlorite on the dioximes is hence similar to that of potassium ferricyanide, with the advantages that the oxidation takes place almost instantaneously and in the cold, that a theoretical yield is obtained, and that the products do not require the tedious purification necessary when ferricyanide is employed.

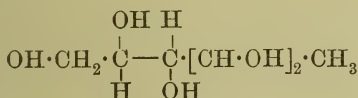
A simple method of preparing carbon tetrabromide consists in dissolving 10 grams of acetone in 10 litres of water, adding 180 grams of bromine and 1500 c.c. of a 30 per cent. solution of sodium hydroxide,

and allowing to remain. It can also be obtained by the action of sodium hypobromite on diacetyldioxime, methylethylketoxime, *iso*-nitrosomethyl ethyl ketone, or *isonitrosocamphor*. It exhibits the following reactions (compare Bolas and Groves, this Journal, 1871, 29, 782). When heated with water in a sealed tube at 200°, it is completely decomposed into carbon dioxide and hydrogen bromide, according to the equation  $\text{CBr}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{HBr}$ . When heated with alcohol in a sealed tube at 150°, carbon tetrabromide yields ethyl bromide, bromoform, and traces of acetaldehyde; when 80 per cent. alcohol is used, the action begins at 100°. With sodium ethoxide in ethereal solution, carbon tetrabromide gives ethyl orthocarbonate. When heated with aniline, carbon tetrabromide yields aniline hydrobromide, whilst with aniline and alcoholic potassium hydroxide solution phenylcarbylamine is obtained. Phenylhydrazine hydrobromide may be readily prepared by adding phenylhydrazine to an ethereal solution of carbon tetrabromide cooled in ice; if alcoholic potassium hydroxide is present, phenylcarbylamine is formed.

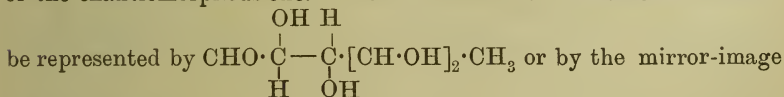
T. H. P.

**Rhodeitol.** EMIL VOTOČEK and J. BULÍK (*Zeit. Zuckerind. Böhm.*, 1906, 30, 333—339).—Rhodose, previously prepared from convolvulin (Abstr., 1900, i, 332) may be more cheaply obtained by heating powdered jalap resin (*Resina jalapae e radice ponderosa*) with barium hydroxide solution to dissolve the glucoside and leave the resin unchanged, removing the barium hydroxide, and hydrolysing by means of 10 per cent. sulphuric acid solution.

*Rhodeitol*,  $\text{C}_6\text{H}_{14}\text{O}_5$ , best prepared by reducing rhodose by means of 2·5 per cent. sodium amalgam in a solution kept alkaline to an extent not exceeding 0·5 per cent. of sodium hydroxide, crystallises from alcohol in silky, white plates melting at 153·5° and is readily soluble in water; it can be distilled, reduces Fehling's solution, and has  $[\alpha]_D - 1·45^\circ$  in aqueous solution or  $-4·6^\circ$  in 10 per cent. borax solution at 21°. Oxidation of rhodeitol by means of bromine in sodium carbonate solution or of nitric acid yields a ketose (rhodeoketose) but no aldose. Rhodeitol is not oxidised by the sorbose bacterium (compare Bertrand, Abstr., 1898, i, 550), so that it must have either the formula



or the enantiomorphous one. The constitution of rhodose must hence



of this formula.

A mixture of equal proportions of the two optical antipodes, rhodose and fucose, gives on reduction with sodium amalgam a true racemic compound, *r-rhodeitol* or *r-fucitol*,  $\text{C}_6\text{H}_{14}\text{O}_5$ , which crystallises in shining plates melting at 168° and dissolves readily in water and sparingly in alcohol.

T. H. P.



The almost complete Conversion into Maltose of the Dextrins obtained by the Saccharification of Starch. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1906, 142, 1216—1218. Compare Maquenne and Roux, this vol., i, 327).—At a temperature of 50°, starch is almost completely converted into maltose by the action of malt extract, and the second stage of the reaction, namely, the conversion of the dextrin into maltose, is accelerated by adding acid until the liquid is neutral to methyl-orange. Under these conditions, 300 c.c. of a solution containing 13 grams of starch and 50 c.c. of a 10 per cent. malt extract yielded after ninety-four hours 103·8 grams of maltose per 100 grams of starch, or 1·7 per cent. less than the theoretical quantity; the solution contained 1·9 per cent. of dextrin which had escaped saccharification owing to the dilution. If, however, the dextrin is precipitated by alcohol and then subjected to the further action of malt extract, it is slowly converted into maltose.

M. A. W.

Combinations of Mercuric Iodide and Methylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1906, 142, 1199—1202. Compare Abstr., 1905, i, 574).—Mercuric iodide readily combines with gaseous methylamine at the ordinary temperature to form the liquid  $5\text{NH}_2\text{Me}, \text{HgI}_2$ , which by loss of methylamine forms successively the solid compounds  $2\text{NH}_2\text{Me}, \text{HgI}_2$  and  $\text{NH}_2\text{Me}, \text{HgI}_2$ .

*Pentamethylaminomercuric iodide*,  $5\text{NH}_2\text{Me}, \text{HgI}_2$ , most conveniently prepared in a pure state by the action of methylamine on the compound,  $2\text{NH}_2\text{Me}, \text{HgI}_2$ , forms a colourless liquid which solidifies at  $-46^\circ$ , can be preserved indefinitely in sealed tubes, but loses methylamine when exposed to the air, the dissociation pressure at  $0^\circ$  being 280 mm. and becoming atmospheric at  $25^\circ$ .

*Dimethylaminomercuric iodide*,  $2\text{NH}_2\text{Me}, \text{HgI}_2$ , obtained from the preceding compound by partial loss of methylamine, or by adding an excess of methylamine solution to a saturated solution of mercuric iodide in potassium iodide, forms colourless prisms sometimes 10 cm. long, with an ammoniacal odour.

*Methylaminomercuric iodide*,  $\text{NH}_2\text{Me}, \text{HgI}_2$ , is obtained from the preceding compound by subjecting it at the ordinary temperature to a current of air for twelve hours, or by placing a capsule containing a weighed quantity of the compound,  $2\text{NH}_2\text{Me}, \text{HgI}_2$ , in a closed vessel containing mercuric iodide, or by pouring a solution of methylamine into excess of a saturated solution of mercuric iodide in potassium iodide; the compound is a yellowish-white solid which yields red mercuric iodide on prolonged exposure to the air.

M. A. W.

Synthesis of Secondary Mixed Amines by Hinsberg's Method. A. MULDER (*Rec. trav. chim.*, 1906, 25, 104—107).—The author has prepared methylpropylamine, ethylpropylamine, and ethylisopropylamine by the general method described by Hinsberg (Abstr., 1892, i, 64). Good yields were obtained except in the case of ethylisopropylamine, and it appears that Hinsberg's method is not suited to the preparation of mixed amines containing a secondary carbon atom. *Benzenesulphonmethylpropylamide*,  $\text{SO}_2\text{Ph}\cdot\text{NMePr}^a$ , obtained by the action of propyl iodide on the potassium derivative of benzenesulphon-

methanamide,  $\text{SO}_2\text{Ph}\cdot\text{NMeK}$ , is a colourless oil and boils at  $184\text{--}186^\circ$  under 21 to 24 mm. pressure. *Benzenesulphonethylpropylamide*, similarly obtained, boils at  $229\text{--}231^\circ$  under 26 to 33 mm. pressure. *Benzenesulphonethylisopropylamide* is crystalline, melts at  $51\text{--}52^\circ$ , and is readily soluble in the usual solvents with the exception of water and light petroleum. T. A. H.

**Action of Ethylenediamine on Cobalt and Platinum Compounds.** HERMANN GROSSMANN and BERNHARD SCHÜCK (*Ber.*, 1906, 39, 1896—1901).—Werner and Bräunlich (*Abstr.*, 1900, i, 86), by the action of varying amounts of potassium thiocyanate on dichlorodiethylenediamine cobaltchloride, have prepared the isomerides  $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{S}\cdot\text{C}\text{:}\text{N})_2]\text{Cl}$  and  $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{N}\cdot\text{C}\text{:}\text{S})_2]\text{Cl}$ , the existence of which depends on the tautomerism exhibited by thiocyanic acid. The authors have prepared compounds of the isothiocyano-series by a simpler method than Werner and Bräunlich's and quite free from the isomeric thiocyano-salts by passing air through an aqueous solution of a mixture of ethylenediamine (2 mols.) and cobalt thiocyanate (1 mol.) on a boiling water-bath until the solution becomes carmine-red. Glistening, ruby-red needles of the diisorhodanato-salt, previously described by Werner and Bräunlich, separate.

*Triethylenediamine cobaltthiocyanate*,  $(\text{Co}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_3$ , prepared by heating an aqueous solution of ethylenediamine (3 mols.) and cobalt thiocyanate (1 mol.), forms golden-yellow, glistening crystals and melts at  $211^\circ$ . It gives the characteristic coloration with ferric chloride. On the addition of potassium cyanide, the solution becomes yellowish-red and, on cooling, the luteocyanide separates in cubical crystals melting at  $240^\circ$ .

The *bromide*,  $(\text{Co}, 3\text{C}_2\text{H}_8\text{N}_2)\text{Br}_3\cdot 2\text{H}_2\text{O}$ , prepared by the action of ethylenediamine (2 mols.) on cobalt bromide (1 mol.), forms yellow needles and melts and decomposes at  $271^\circ$ .

*Dibromodiethylenediamine cobaltthiocyanate*,  $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2]\text{SCN}\cdot\text{H}_2\text{O}$ , prepared by the action of potassium thiocyanate on a cold saturated solution of the praseobromide,  $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{Br}_2]\text{Br}$ , forms green crystals, the aqueous solution of which changes from green to red when boiled with water.

The *compound*,  $[\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2](\text{SCN})_2$ , prepared by the action of ethylenediamine on potassium platinic thiocyanate,  $\text{K}_2\text{Pt}(\text{SCN})_6$ , forms yellow crystals and melts at  $141^\circ$ .

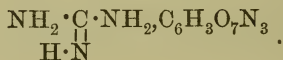
The *compound*,  $[\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)_2](\text{SCN})_2$ , prepared in an analogous manner from potassium platinous thiocyanate,  $\text{K}_2\text{Pt}(\text{SCN})_4$ , forms orange-yellow crystals and melts at  $177^\circ$ . A. McK.

**Bromodialkylacetamides.** KALLE & Co. (D.R.-P. 166359).—Bromodiethylacetamide,  $\text{CEt}_2\text{Br}\cdot\text{CO}\cdot\text{NH}_2$  or  $\text{CEt}_2\text{Br}\cdot\text{C}(\text{NH})\cdot\text{OH}$ , was prepared by adding very slowly the calculated amount of bromine to diethylacetamide dissolved in water; the product is extracted with ether recrystallised from dilute alcohol. A similar bromo-derivative was obtained from ethylpropylacetamide. G. T. M.

**Hydroxymethyl Derivatives of Amides.** ALFRED EINHORN (D.R.-P. 162395. Compare Abstr., 1905, i, 646; this vol., i, 245).—The method of preparation of hydroxymethyl derivatives from aromatic amides is not applicable to fatty amides unless containing substituted halogen. Thus, chloroacetamide readily reacts at 100° with formaldehyde in presence of concentrated hydrochloric acid. The product is evaporated in a vacuum after neutralising with sodium acetate, and the resulting syrup crystallised from acetone.

C. H. D.

**Probable Stereoisomerism of Nitrogen in Guanidine Picrate.** VICTOR VON CORDIER (*Chem. Centr.*, 1906, i, 340; from *Verh. Ges. Deut. Naturforsch. Aerzte*, 1904, ii, 105—108).—Guanidine picrate is usually obtained in the form of dark yellow plates which, owing to repeated twinning, have a hook-like structure, but when guanidine which has been prepared by the decomposition of methyl guanidine sulphate by means of barium hydroxide is used, the picrate crystallises in rosettes of bright yellow needles. Both forms have the same composition, temperature of decomposition, sp. gr., and electrical conductivity, but whilst 100 parts water dissolve 0.037 part of the plates at 0°, 0.061 at 20°, and 0.574 at 80°, the solubility of the needles is 0.043, 0.060, and 0.800 at these temperatures respectively. One form cannot be obtained from the other by crystallisation. When either is converted into the carbonate or other salt, or even into derivatives such as glycocyamine, guanidinesarcosine hydrochloride, &c., and the picrate again prepared, it usually crystallises in the original form. Under certain conditions, however, it is possible to obtain the crystalline plates from the carbonate or glycine compound which has been prepared from needles of the picrate, but the reverse change has not been observed. Both forms are optically inactive, and are probably stereoisomerides, the plates being the stable modification

$$\text{NH}_2 \cdot \underset{\text{N} \cdot \text{H}}{\underset{|}{\text{C}}} \cdot \text{NH}_2, \text{C}_6\text{H}_3\text{O}_7\text{N}_3,$$


E. W. W.

**Preparation of Hydrogen Cyanide from Ferrocyanides.** WALTHER FELD (D.R.-P. 162362).—Sufficient calcium hydroxide or carbonate is added to a solution of calcium ferricyanide to combine with all the iron present; mercuric chloride is then added, together with magnesium chloride, to prevent the precipitation of mercuric oxide, and the whole is boiled. The reaction is  $\text{Ca}_3(\text{FeCy}_6)_2 + 3\text{Ca}(\text{OH})_2 + 6\text{HgCl}_2 = 6\text{HgCy}_2 + 6\text{CaCl}_2 + \text{Fe}_2(\text{OH})_6$ . The precipitate is filtered off and the solution distilled with sulphuric acid. Ferrocyanides are previously oxidised to ferricyanides with bleaching powder and sulphuric acid.

C. H. D.

**Reduction of Potassium Ferricyanide.** DOMENICO VENDITORI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 370—373).—Potassium ferri-



cyanide is reduced by hydrogen sulphide, slowly at the ordinary temperature, rapidly on heating, the reaction being expressed by the equation  $6K_3FeCy_6 + 3H_2S = 4K_4FeCy_6 + K_2Fe_2Cy_6 + 6HCN + 3S$ . These results differ from those obtained by Williamson (*Annalen*, 1846, 57, 237).

T. H. P.

**Ferricyanides of Mercury**, GUSTAVE FERNEKES (*J. Amer. Chem. Soc.*, 1906, 28, 602—605).—*Mercuric ferricyanide*,  $Hg_3Fe_2(CN)_{12}$ , obtained by adding a concentrated aqueous solution of potassium ferricyanide to a solution of mercuric chloride in alcohol and ether and washing the precipitate with alcohol and ether, is a bright yellow substance which is fairly stable when dry, but rapidly undergoes decomposition in aqueous solution with formation of hydrogen cyanide and a blue substance, which is probably Prussian blue.

*Mercurous ferricyanide*,  $Hg_3Fe(CN)_6$ , is obtained as a flocculent, cream-coloured precipitate when a solution of mercurous nitrate is added to a solution of potassium ferricyanide, and turns blue on exposure to the air.

E. G.

**Oxidation of Chromous Salts**. JULIUS SAND and O. BURGER (*Ber.*, 1906, 39, 1771—1779. Compare Abstr., 1903, ii, 549; 1904, ii, 39; Kohlschütter, *ibid.*, ii, 737).—When nitric oxide is passed into a moist amyl-alcoholic solution of chromous thiocyanate and excess of ammonium thiocyanate, an opaque, dark red solution is obtained which can be concentrated on the water-bath. After removal of the alcohol, the purple residue is recrystallised from hot concentrated ammonium hydroxide; it separates in glistening needles which have the composition  $O[Cr(SCN)_2]_2 \cdot 4NH_3$ . The ammonia is only loosely bound, being eliminated by dilute hydrochloric acid, and from the conductivity and cryoscopic behaviour of the solution the residual,  $Cr_2(SCN)_4O$ , functions as a binary electrolyte. Nitrous acid precipitates unstable black crystals from an ice-cold solution of the substance in dilute sulphuric acid. From a dilute hydrochloric acid solution, pyridine and water precipitate violet-grey crystals having the composition  $Cr_2(SCN)_4O(C_5H_5N)_4$ .

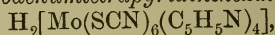
When the oxidation of the amyl-alcoholic solution of chromous thiocyanate and excess of ammonium thiocyanate is performed in the presence of pyridine by nitric oxide, ammonium persulphate, or alcoholic iodine, a very stable substance,  $Cr(SCN)_4(C_5H_5N)_2 \cdot H(C_5H_5N)$ , is obtained, which is not attacked by acidified hydrogen peroxide or by chlorine and boiling hydrochloric acid. With alcoholic pyridine, it forms a substance,  $[Cr(SCN)_4(C_5H_5N)_2(C_5H_5N)]H(C_5H_5N)$ , in harmony with the co-ordination theory.

The action of nitric oxide on chromous salts in ammonium carbonate solution leads to the formation of a basic chromammonium carbonate,  $Cr(NH_4)(OH)_2CO_3$ .

C. S.

**Reduction of Molybdic Acid in Thiocyanic Acid Solution**. JULIUS SAND and O. BURGER (*Ber.*, 1906, 39, 1761—1770. Abstr., 1905, i, 923; Chilesotti, this vol., ii, 263, 365).—Through a solution of ammonium molybdate and excess of ammonium thiocyanate in

dilute hydrochloric acid a current of 1.95 amperes is passed until two farads have been utilised for each gram-mol. of molybdic acid, the platinum cathode being smooth and of 300 sq. cm. area. The reduced liquid is treated with ether, pyridine added until the ethereal layer is colourless, the red oil is separated and boiled with alcohol. The brown, crystalline residue is described subsequently. The alcoholic solution by treatment with excess of ether deposits a yellow oil, soluble in ammonium hydroxide and reprecipitated by cold acid in yellow crystals of *molybdenumtetrapyridinehexathiocyanic acid*,



which readily loses pyridine and is best purified by precipitation from potash solution by carbon dioxide. When treated with pyridine in methyl-alcoholic solution, it yields the hexathiocyanate previously described (*loc. cit.*). After the action of hydrogen chloride on the acid in acetone, ether precipitates amber-yellow crystals of the composition  $\text{Mo}(\text{SCN})_6(\text{C}_5\text{H}_5\text{N})_4\text{H}_2(\text{C}_5\text{H}_5\text{N})_2\cdot 2\text{HCl}$ , which melt at  $141^\circ$ .

The *zinc*, *nickel*, and *copper* salts precipitated from ammoniacal solution contain  $(\text{NH}_3)_4$  in the place of  $(\text{C}_5\text{H}_5\text{N})_4$ ; the zinc salt,  $\text{Zn}[\text{Mo}(\text{SCN})_6(\text{NH}_3)_4]$ , crystallises from hot concentrated ammonium hydroxide in glistening needles and is especially characteristic. The *silver* salt,  $\text{Ag}_2[\text{Mo}(\text{SCN})_6(\text{C}_5\text{H}_5\text{N})_4]$ , is precipitated from methyl-alcoholic and pyridine solution in yellow crystals.

Evidence is quoted which indicates that the molybdenum in these compounds functions as a quadrivalent element.

The brown crystals previously mentioned separate from hot alcohol in aggregates of brown, feathery crystals which melt and decompose at  $182^\circ$ . They were previously described as having the composition  $\text{Mo}[(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_4]$  (*loc. cit.*), but are now found to be  $\text{Mo}(\text{OH})_2(\text{SCN})_3(\text{C}_5\text{H}_5\text{N})_2$ . The chloride is  $\text{MoOCl}_3(\text{C}_5\text{H}_5\text{N}, \text{HCl})_2$ , not  $\text{Mo}(\text{C}_5\text{H}_5\text{N}, \text{HCl})_6\text{Cl}_4$  (*loc. cit.*), and is easily hydrolysed in dilute alcohol to a basic salt,  $\text{Mo}(\text{OH})_3\text{Cl}_2\cdot\text{C}_5\text{H}_5\text{N}$ . The brown molybdenum-dihydroxydipyridinetriithiocyanate does not react with atmospheric oxygen; with 20 per cent. sulphuric acid, it forms a purple solution from which dark green crystals,  $[\text{Mo}(\text{OH})(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_3]_2\text{SO}_4$ , separate.  
C. S.

**New Methods of preparing some Organic Derivatives of Arsenic.** VICTOR AUGER (*Compt. rend.*, 1906, 142, 1151—1153. Compare Abstr., 1904, i, 22, 724, 983).—Starting with methylarsonic acid or cacodylic acid, which are commercial products, the following organic derivatives of arsenic can be readily prepared: methylarsine di-iodide,  $\text{AsMeI}_2$ , obtained by reducing methylarsonic acid with sulphur dioxide and treating the product with potassium iodide and hydrochloric acid, the yield is 82 per cent. of the theoretical, and it is converted quantitatively into methylarsine oxide,  $\text{AsMeO}$ , by heating a solution in benzene with dry sodium carbonate; methylarsine dichloride,  $\text{AsMeCl}_2$ , prepared by adding methylarsonic acid to phosphorus trichloride, contains a small quantity of arsenic trichloride; cacodyl chloride,  $\text{AsMe}_2\text{Cl}$ , obtained with an excellent yield by distilling a mixture of sodium hypophosphite, cacodylic acid, and hydrochloric acid,  $2\text{AsMe}_2\text{O}_2\text{H} + 3\text{H}_3\text{PO}_2 + 2\text{HCl} = 3\text{H}_3\text{PO}_3 + \text{H}_2\text{O} + 2\text{AsMe}_2\text{Cl}$ , or



by the action of phosphorus trichloride on cacodylic acid, is converted into cacodylic oxide by the action of dry sodium carbonate; cacodyl,  $\text{As}_2\text{Me}_4$ , is readily prepared by the action of excess of sodium hypophosphite on cacodylic acid in hydrochloric acid solution; tetramethylarsonium iodide,  $\text{AsMe}_4\text{I}$ , obtained by the action of hypophosphorus acid and methyl iodide on cacodylic acid according to the equation  $\text{AsMe}_2\text{O}_2\text{H} + 2\text{MeI} + 2\text{H}_3\text{PO}_2 = \text{AsMe}_4\text{I} + 2\text{H}_3\text{PO}_3 + \text{HI}$ .

M. A. W.

**Preparation and Properties of Individual Organo-magnesium Compounds.** WLADIMIR TSCHELINZEFF (*Chem. Zeit.*, 1906, 30, 378—379. Compare this vol., ii, 334, 335).—Magnesium alkyl compounds of the type  $\text{R}\cdot\text{Mg}\cdot\text{R}$  are solid substances which decompose on heating without melting; they are soluble in a mixture of ether and benzene, and can be recovered from this solution unchanged. They catch fire and explode in contact with water, carbon dioxide, or oxygen, and react with ketones, aldehydes, or esters to form complex substances which are decomposed by water with the formation of hydrocarbons. Compounds of the type  $\text{RMgI}$  are solids which dissolve in ether or a mixture of ether and benzene, but cannot be recovered from the solution; they react less violently with water, carbon dioxide, or oxygen, and with ketones, aldehydes, or esters they yield compounds which do not evolve hydrocarbons on treatment with water.

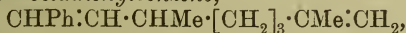
P. H.

**Problem of Substitution in the Benzene Ring.** ARNOLD F. HOLLEMAN (*Chem. Centr.*, 1906, i, 457—459; from *Chem. Weekblad*, 3, 1—11. Compare Abstr., 1903, i, 336, 623; 1904, i, 486; 1905, i, 41, 42, 515).—The problem of substitution in the benzene ring is discussed at length in the abstract, and some of the work of the author published already on the nitration of benzene derivatives is quoted. For further details, the abstracts or original paper should be consulted.

E. W. W.

**Optically Active Benzene Hydrocarbons. III.** AUGUST KLAGES and RICHARD SAUTTER (*Ber.*, 1906, 39, 1938—1942. Compare Abstr., 1904, i, 302; 1905, i, 579).— $\alpha$ -Hydroxy- $\gamma\gamma$ -dimethyl- $\Delta^7$ -octenylbenzene,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHMe}\cdot[\text{CH}_2]_3\cdot\text{CMe}\cdot\text{CH}_2$ , prepared by the action of acetic acid and ice on the product of the reaction of magnesium phenyl bromide with citronellaldehyde, is a colourless oil, which boils at  $174^\circ$  under 9.5 mm. pressure, has a sp. gr. 0.9469 at  $15.5^\circ/4^\circ$ ,  $n_D$  1.5137 at  $15.5^\circ$ , and  $[\alpha]_D - 1.56^\circ$  at  $15.5^\circ$ . The carbinol obtained on treatment of the reaction product with ice only has a higher specific rotation.

$\gamma\gamma$ -Dimethyl- $\Delta^{\alpha\gamma}$ -octadienylbenzene,



is formed by treating the carbinol with hydrogen chloride in ethereal solution cooled by ice, and heating the dichloride,  $\text{C}_{16}\text{H}_{24}\text{Cl}_2$ , so formed, which has  $n_D$  1.5168 and  $[\alpha]_D - 9.06^\circ$  at  $11.5^\circ$ , with pyridine for five hours. It is a colourless, odourless, strongly refracting oil, which boils at  $152^\circ$  under 9.5 mm. pressure, has a sp. gr. 0.8947 at  $17^\circ/4^\circ$ ,

$n_D$  1.5276, and  $[\alpha]_D - 65.11^\circ$  at  $17^\circ$ , and reacts with bromine in the cold, forming an oily *tetrabromide*,  $C_{16}H_{22}Br_4$ , together with small amounts of bromo-derivatives.

When heated with oxalic acid, the carbinol yields 1-*phenyl-5-methyl-2-isopropenylcyclohexane*,  $C_6H_9MePh \cdot CMe \cdot CH_2$ ; this is obtained as a colourless, mobile oil, which boils at  $139-140^\circ$  under 10 mm. pressure, has a sp. gr. 0.9462 at  $15.7^\circ/4^\circ$ ,  $n_D$  1.5802, and  $[\alpha]_D + 17^\circ$ .

$\gamma\gamma$ -*Dimethyl- $\Delta^7$ -octenylbenzene*,  $C_{16}H_{24}$ , is formed by reduction of  $\gamma\gamma$ -dimethyl- $\Delta^{7,8}$ -octadienylbenzene by means of sodium and alcohol, boils at  $145-146^\circ$  under 9.5 mm. pressure, has a sp. gr. 0.8844 at  $11.5^\circ/4^\circ$ ,  $n_D$  1.5029, and  $[\alpha]_D - 7.26^\circ$ .

$\gamma\gamma$ -*Dimethyloctylbenzene*,  $C_{16}H_{26}$ , prepared by reducing the preceding substance with hydriodic acid and red phosphorus in a sealed tube at  $160^\circ$ , is obtained as a colourless, miscible oil which boils at  $275^\circ$  (corr.) or at  $140^\circ$  under 8.5 mm. pressure, and has a sp. gr. 0.8789 at  $10.5^\circ/4^\circ$ ,  $n_D$  1.4960, and  $[\alpha]_D - 1.82^\circ$  at  $10.5^\circ$ . When treated with sulphuric acid containing 6 per cent. of sulphuric anhydride, it yields an oily *sulphonic acid*, which is soluble in water, and with sodium chloride gives a voluminous precipitate of the *sodium salt*. G. Y.

**Bromination of Toluene.** F. H. VAN DER LAAN (*Chem. Centr.*, 1906, i, 661—662; from *Chem. Weekblad*, 1906, 3, 15—21).—The author has made quantitative measurements with a view to determining the influence of temperature, of bromine carriers, or of light on the yield of *o*- or *p*-bromotoluene or benzyl bromide. Below  $17^\circ$ , no benzyl bromide is formed, whereas above  $83^\circ$  it is formed exclusively. Antimony tribromide only slightly increases the yield of ring-substituted derivatives, and appears rather to favour the formation of the para-form. Five mg. of aluminium added to 3 c.c. of bromine completely prevent the formation of benzyl bromide, and increase the yield of the *o*-variety as compared to the *p*-, whereas 2 mg. of aluminium are without effect. Ferric bromide has a similar although rather more marked effect than aluminium bromide. The action of aluminium amalgam is similar to that of aluminium bromide. The addition of 0.02 mol. of phosphorus pentabromide to 1 mol. of bromine gives, at  $50^\circ$ , 10 per cent. more benzyl bromide than in the absence of a halogen carrier. In diffused daylight, bromination takes place more rapidly. A reaction which at  $25^\circ$  is not completed in the dark after a week, is effected in ten minutes in daylight. Benzyl bromide is formed in this case, together with small quantities of more highly brominated derivatives. Pure benzyl bromide is obtained by dropping bromine into eight times its weight of toluene kept at  $80^\circ$ . P. H.

**Preparation of Aromatic Sulphonamates by Reduction of Nitro-derivatives with Sodium Hyposulphite.** ALPHONSE SEYEWETZ and BLOCH (*Compt. rend.*, 1906, 142, 1052—1054).—A mixture of nitrobenzene (63 grams), trisodium phosphate (75 grams), and sodium hyposulphite (380 grams) is made, and to it a litre of boiled water is added, and the whole vigorously shaken for some minutes and then set aside. After twenty-four hours, a quantity of sodium phenylsulphonamate will have separated; a second fraction

may be obtained by cooling the mother liquor to  $0^{\circ}$ , and a third by then evaporating the mother liquor to dryness and extracting the residue with alcohol. The yield of the sodium salt is about equal to that of the nitrobenzene taken. The process is also applicable to the preparation of the corresponding sulphonamates from the three nitrotoluenes, *m*-nitro-xylene, and  $\alpha$ -nitronaphthalene. T. A. H.

**Additive Compounds of Aromatic Hydrocarbons with Polynitro-derivatives.** GIUSEPPE BRUNI and L. FERRARI (*Chem. Zeit.*, 1906, 30, 568—569).—The authors have prepared additive compounds of diphenyl, diphenylmethane, triphenylmethane, dibenzyl, stilbene, tolane, and azobenzene with picryl chloride, and find that the number of molecules of the latter compound which combines with one molecule of the hydrocarbon is proportional to the number of benzene rings contained in the hydrocarbon. P. H.

**Constitutional Formula of 1:2-Dinitrosonaphthalene.** GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1906, 41, 588—591).—Contrary to the statement of Koreff (*Abstr.*, 1886, 363), 1:2-dinitrosonaphthalene can be reduced by means of tin and hydrochloric acid, yielding naphthafurazan (Goldschmidt and Schmidt, *Abstr.*, 1884, 1359) and 1:2-naphthylenediamine. The author hence regards 1:2-dinitrosonaphthalene as  $\beta$ -naphthaquinonedioxime peroxide,  $C_{10}H_6 \begin{smallmatrix} \text{N}\cdot\text{O} \\ \text{N}\cdot\text{O} \end{smallmatrix}$ .

Oxidation of this compound in concentrated sulphuric acid solution by means of nitric acid of sp. gr. 1.52 yields the *dinitro*-derivative,  $C_{10}H_4(NO_2)_2 \cdot N_2O_2$ , which crystallises from acetic acid in yellow prisms melting at  $212^{\circ}$ , is moderately soluble in ethyl acetate or nitric acid, and dissolves in alkali solution, giving a red coloration.

T. H. P.

**Synthesis of Alkyl Derivatives of 2:4-Dinitroaniline and of Two *iso*Propyl-2:4:6-Trinitroanilines.** A. MULDER (*Rec. trav. chim.*, 1906, 25, 108—116).—The author prepared a number of these alkyl derivatives by Clemm's method (*J. pr. Chem.*, 1869, 108, 320, and 1870, ii, 1, 170), which consists in treating 1-bromo-2:4-dinitrobenzene with the appropriate amine. Negative results, however, were obtained with diisopropylamine and ethylisopropylamine, due probably to the influence of the secondary carbon atom in the *isopropyl* groups.

2:4-Dinitromethylpropylaniline,  $C_6H_3(NO_2)_2NPr^aMe$ , obtained by the action of methylpropylamine on the bromodinitrobenzene, forms bright yellow, prismatic crystals, melts at  $71-72^{\circ}$ , and is readily soluble in acetone or warm alcohol. 2:4-Dinitroethylpropylaniline, prepared similarly, separates from methyl alcohol in small, flattened, prismatic, yellow crystals and melts at  $54-55^{\circ}$ . 2:4-Dinitrophenylbenzylmethylamine crystallises from hot alcohol in bright yellow spangles, melts at  $143-144^{\circ}$ , and is readily soluble in benzene, acetone, or warm alcohol, less so in chloroform or ether. 2:4-Dinitrophenylbenzylethylamine separates from ether in large, bright yellow, transparent crystals and melts at  $72-73^{\circ}$  (compare Schultz, Rohde,



and Bosch, Abstr., 1904, i, 992). 2:4-Dinitrophenylbenzylamine separates from a mixture of acetone and alcohol in small, bright yellow, prismatic crystals and melts at 115—116°. 2:4-Dinitrophenyldibenzylamine melts at 104—105° (compare Pinnow and Wiskott, Abstr., 1899, i, 501). 2:4-Dinitrophenylethylaniline melts at 95° (compare Deletra and Ullmann, Abstr., 1904, i, 272). 2:4-Dinitrophenylbenzylaniline, obtained by heating in a closed vessel at 100°, a mixture of 1-bromo-2:4-dinitrobenzene, benzylaniline, and sodium acetate in presence of alcohol, forms small, red crystals from warm acetone and melts at 168°.

2:4-Dinitrophenylpropylaniline is best prepared by heating propylaniline, obtained by Pictet and Crepieux's method (Abstr., 1888, i, 688), with bromodinitrobenzene, dissolved in alcohol, under pressure. It crystallises in brown spangles with a green sheen or in small needles of the same tint, and melts at 73—74°.

When diisopropylamine reacts with bromodinitrobenzene dissolved in alcohol, four products are formed: (1) bright yellow needles melting at 81°, (2) orange prisms melting at 106—107°, (3) prisms resembling those of No. 2, but melting at 89—90°, and (4) yellow spangles melting at 123°. None of these substances can be the 2:4-dinitrodiisopropylaniline expected.

Ethyl isopropylamine reacts very slowly with an alcoholic solution of bromodinitrobenzene, yielding an oil from which no well-defined amine can be isolated. When this oil is treated with picryl chloride, it furnishes 2:4:6-trinitroethylisopropylaniline, which exists in two forms: (1) red needles, and (2) yellow spangles. The first form passes into the second at 90°, and the latter melts at 108—109°.

2:4-Dinitroisopropylaniline crystallises in large, flattened, yellow needles from acetone, and in spangles from warm alcohol, and melts at 94—95°. When added to warm nitric acid of sp. gr. 1.52 and the solution boiled, this substance is converted into van Romburgh's 2:4:6-trinitrophenylisopropylnitroamine, which melts at 107° (compare Abstr., 1886, i, 455).

2:4:6-Trinitroisopropylaniline crystallises from a mixture of alcohol and acetic acid in yellow needles and melts at 106—107°.

T. A. H.

**Oxidation of 2:4-Dinitroanilines with Chromic Anhydride.** A. MULDER (*Rec. trav. chim.*, 1906, 25, 117—120).—Van Romburgh has shown that when 2:4-dinitrodialkylanilines, dissolved in acetic acid, are oxidised with chromic acid, the alkyl groups are successively replaced by hydrogen atoms, and that when two different alkyl groups are present only one of the two possible dinitroalkylanilines is formed (Abstr., 1889, 971; 1896, i, 478). The author oxidised several of the 2:4-dinitrodialkylanilines described in the preceding abstract by van Romburgh's method and found that in most cases in addition to dinitroaniline both possible dinitromonoalkylanilines were produced, although usually one was formed in much larger quantity than the other.

2:4-Dinitrophenyldibenzylamine, on oxidation by chromic acid in presence of acetic acid, yielded 2:4-dinitrophenylbenzylamine in

addition to dinitroaniline, and not the latter only, as Pinnow and Wiskott assert (Abstr., 1899, i, 500).  
T. A. H.

**Hexanitrodiphenylamines.** A. MULDER (*Rec. trav. chim.*, 1906, 25, 121—123).—When 2:4-dinitrophenylmethylaniline is added to nitric acid of sp. gr. 1.49, and, after the first violent action has subsided, the solution is heated to the boiling point for fifteen minutes, *hexanitrodiphenylmethylaniline* is formed. This crystallises from acetic acid in small, yellow spangles and melts at 236—237°, and when boiled with an aqueous solution of potassium hydroxide yields methylamine. *Hexanitrodiphenylethylaniline*, obtained in a similar manner, forms small, colourless needles, becomes brown on exposure to light, and melts at 198—200°. It yields ethylamine when boiled with an aqueous solution of potassium hydroxide, but is resistant to chromic acid, yielding, with the latter, only a small quantity of resinous products. *Hexanitrodiphenylpropylamine* forms small, bright yellow needles and melts at 136—137°. These three substances all give intense red colorations with alkalis.  
T. A. H.

**Hydrogen Phosphites of Primary Cyclic Amines.** PAUL LEMOULT (*Compt. rend.*, 1906, 142, 1193—1195).—When phosphorus trichloride (1 mol.) and aniline (6 mols.) are mixed in ethereal solution, aniline hydrochloride is precipitated, and the resulting mother liquor slowly absorbs water from the air and deposits voluminous white crystals of the acid phosphite of the base; the same product is obtained if chloroform is used as a solvent instead of ether, and the hydration is hastened by warming the solution at 100°. The hydrogen phosphites of the primary cyclic amines are insoluble in ether, chloroform, or benzene, but can be recrystallised from alcohol; they have definite melting points, but decompose at a slightly higher temperature with the formation of the primary base, hydrogen phosphide, and ortho-phosphoric acid. *Hydrogen aniline phosphite*,  $C_6H_5 \cdot NH_2, H_3PO_3$ , forms beautiful pale red or green needles, or large, brilliant crystals which melt at 179°, and is precipitated by alcohol from aqueous solution in the form of small plates melting at 179°. *Hydrogen o-toluidine phosphite*,  $C_7H_7 \cdot NH_2, H_3PO_3$ , forms beautiful, colourless needles which melt at 174° and decompose at 200°. *Hydrogen as-m-xylylidine phosphite*,  $C_8H_9 \cdot NH_2, H_3PO_3$ , crystallises in colourless needles and melts at 172°.  
M. A. W.

**Formation of Salts of Aromatic Bases with Dicarboxylic Acids.** OTTO ANSELMINO (*Chem. Centr.*, 1906, i, 753; from *Ber. Deut. pharm. Ges.*, 15, 422—426. Compare Abstr., 1904, i, 306).—The results of experiments on the behaviour of oxalic and succinic acids towards a further series of aromatic bases have not indicated any regularity either in reference to the possibility of the formation of salts or to the stability of the salts. *o*-Anisidine and *m*-nitroaniline form acid oxalates; *as-m*-xylylidine and *o*- and *m*-aminobenzoic acids, normal oxalates and aniline, *o*-, *m*-, and *p*-toluidines, *p*-anisidine, *p*-phenetidine,  $\psi$ -cumidine, *p*-aminobenzoic acid, and  $\alpha$ - and  $\beta$ -naphthylamines yield both acid and normal oxalates. The acid reaction of the

acid oxalates of *m*- and *p*-toluidines is not affected by boiling with alcohol, but the acid oxalates of aniline, *o*-toluidine, *p*-anisidine, *p*-phenetidine, *p*-aminobenzoic acid, and of  $\alpha$ - and  $\beta$ -naphthylamines become neutral; the acid oxalates of *o*-toluidine, *o*-anisidine, *o*-aminobenzoic acid, *m*- and *p*-nitroaniline, and of  $\alpha$ - and  $\beta$ -naphthylamine form condensation products.

Aniline, *o*- and *p*-toluidine, *o*- and *p*-anisidine, *as-m*-xylidine, and  $\beta$ -naphthylamine form acid succinates.

*o*-Toluidine oxalate melts at 167°, *o*-toluidine hydrogen oxalate at 171°, *as-m*-xylidine oxalate at 167°,  $\psi$ -cumidine oxalate at 183°,  $\psi$ -cumidine hydrogen oxalate at 179°, *m*-aminobenzoic acid oxalate at 246°, *p*-aminobenzoic acid hydrogen oxalate above 275°, *p*-aminobenzoic acid oxalate above 275°, *p*-phenetidine oxalate at 201°, *p*-phenetidine hydrogen oxalate at 201°,  $\beta$ -naphthylamine oxalate at 181°, and  $\beta$ -naphthylamine hydrogen oxalate at 176°.

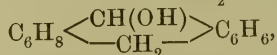
*o*-Toluidine oxalo-*o*-toluidate,  $C_{16}H_{18}O_3N_2$ , melts at 153°; oxalo-*o*-anisic acid,  $C_9H_9O_4N$ , at 159°; *m*-nitro-oxanilic acid,  $C_8H_6O_5N_2$ , at 158°, and ethyl *p*-nitro-oxanilate,  $C_{10}H_{10}O_5N_2$ , at 168°.  $\beta$ -Naphthylamine  $\beta$ -naphthylloxamate,  $C_{22}H_{22}O_3N_2$ , is also a condensation product.

E. W. W.

**Influence of Catalysts on the Formation of Anilides. II.** NICOLAI A. MENSCHUTKIN (*Chem. Centr.*, 1906, i, 551; from *Iswiestja Petersburg Polytechn. Inst.*, 1905, 4, 181—190. Compare Abstr., 1903, i, 813).—The accelerating influence of hydrogen chloride, bromide, or iodide on the rate of acetylation of aniline, *o*-, *m*-, or *p*-toluidine, and *m*- or *p*-xylidine by acetic acid was found to be proportional to the molecular weight of the acid and to the quantity employed. In the presence of these acids, the reaction was uni-molecular, otherwise it was bi-molecular. A methyl group in the ortho-position decreases the velocity of acetylation, whereas in the meta- or para positions it increases it.

P. H.

**Some Hydroanthracene Derivatives.** MARCEL GODCHOT (*Compt. rend.*, 1906, 142, 1202—1204. Compare Abstr., 1904, i, 987; 1905, i, 201).—Octahydroanthranol,  $C_6H_{10}$   $\begin{matrix} \text{CH(OH)} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{matrix}$   $C_6H_4$  or



obtained by reducing hexahydroanthrone by means of sodium and alcohol, crystallises in small, yellow needles, melts at 81—82°, is very soluble in the ordinary solvents, and loses  $H_2O$  on distillation even in a vacuum to form a hexahydroanthracene; the *phenylurethane*,  $C_{14}H_{17}O \cdot CO \cdot NHPh$ , crystallises from acetone in beautiful, colourless needles which melt at 151—152°.

$\beta$ -Hexahydroanthracene, isomeric with the compound described by Graebe and Liebermann (Abstr., 1882, 857), obtained from octahydroanthranol either by distillation or by boiling it in alcoholic solution with a few drops of hydrochloric acid, or by heating it with acetic or benzoic anhydride or chloride, crystallises in small, colourless plates;



it melts at  $66.5^{\circ}$ , boils at  $303-306^{\circ}$ , is insoluble in water, soluble in hot alcohol, acetic acid or benzene, the solutions exhibiting a beautiful blue fluorescence. It yields dihydro-oxanthranol on oxidation, and reacts with chlorine or bromine to form dichloro- or dibromo-octahydroanthracene identical with the compounds similarly obtained from octahydroanthracene (Abstr., 1904, i, 987);  $\beta$ -hexahydroanthracene has therefore the formula  $C_6H_{10} \begin{smallmatrix} & CH \\ & | \\ C_6H_4 & & CH \\ & | \\ & CH \end{smallmatrix} C_6H_4$  or  $C_6H_8 \begin{smallmatrix} & CH \\ & | \\ C_6H_8 & & CH \\ & | \\ & CH \end{smallmatrix} C_6H_6$ .

9 : 10-*Tetrahydroanthracene*,  $C_6H_6 \begin{smallmatrix} & CH_2 \\ & | \\ C_6H_4 & & CH_2 \\ & | \\ & CH_2 \end{smallmatrix} C_6H_4$ , obtained by reducing dihydro-oxanthranol by means of hydrogen iodide, forms colourless plates which melt at  $101^{\circ}$ , is readily soluble in the ordinary reagents, and the solutions are not fluorescent; it yields dihydro-oxanthranol on oxidation, and readily forms substitution products with chlorine or bromine. 9 : 10-*Dibromotetrahydroanthracene*,  $C_6H_6 \begin{smallmatrix} & CHBr \\ & | \\ C_6H_4 & & CHBr \\ & | \\ & CHBr \end{smallmatrix} C_6H_4$ , crystallises in large, yellow needles, melts at  $169^{\circ}$ , and is not attacked by aqueous or alcoholic potassium hydroxide at  $250^{\circ}$ .

M. A. W.

**Phenol.** HUGO KÜHL (*Chem. Centr.*, 1906, i, 344—345; from *Pharm. Zeit.*, 50, 1001).—When phenol which has been kept for a long time and has become red is distilled, a solid, violet-red residue remains, which is insoluble in water or ammonia. By the action of hydrogen peroxide on an ammoniacal solution of phenol, a green coloration is formed after some time. No characteristic coloration is formed when sodium nitrite is added to a solution of phenol in concentrated sulphuric acid. When heated with a solution of ferric chloride and evaporated on the water-bath, a residue is left which has a faint red tinge.

E. W. W.

**Aluminium Phenoxide.** ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1906, 28, 608—617).—A method is described for the preparation of aluminium phenoxide,  $Al(OPh)_3$  (Gladstone and Tribe, *Trans.*, 1882, 41, 5). The compound is a grey, translucent, brittle solid which melts at  $265^{\circ}$ , has a vitreous lustre, a sp. gr. 1.23, and is soluble in hot benzene, toluene, or xylene, and also in dry alcohol, chloroform, carbon disulphide, or acetone. The compound is decomposed by water with formation of aluminium hydroxide. It reacts with bromine with production of tribromophenol bromide. When aluminium phenoxide is treated with nitric acid, *o*-nitrophenol, 1 : 2 : 4-dinitrophenol, and picric acid are produced. The substance reacts with alcohol with formation of aluminium ethoxide and phenol, and also with ether with production of aluminium ethoxide and phenetole. The action of several other reagents is described. Aluminium phenoxide is decomposed by heat with formation of benzene, phenol, phenyl ether, and some higher boiling substances which have not been identified. This decomposition affords a good method for the preparation of phenyl ether.

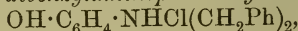
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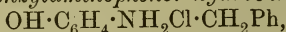
**5-Nitro-2-aminophenol.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 165650).—5-Nitro-2-aminophenol is readily obtained by dissolving ethenyl-*o*-aminophenol in cold concentrated sulphuric acid and nitrating with a mixture of this acid and nitric acid. The nitroethyl-*o*-aminophenol thus produced is boiled with an equal weight of hydrochloric acid until solution is complete, when 5-nitro-2-aminophenol is precipitated on neutralising the solution with sodium or calcium carbonate. G. T. M.

**Action of Benzyl Chloride on Aminophenols** MARUSSIA BAKUNIN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 361—375).—When *p*-aminophenol and benzyl chloride are heated together in alcoholic solution in presence of zinc, an organo-zinc chloro-compound melting at 240° is obtained, which, on decomposition with water, gives rise to benzylaminophenol hydrochloride melting at 224°.

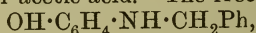
The interaction of *p*-aminophenol and benzyl chloride in alcoholic solution yields: (1) *p*-dibenzylaminophenol hydrochloride,



which crystallises from alcohol in short, colourless, monoclinic prisms melting at 200—224°, and is almost insoluble in the ordinary organic solvents; water dissolves it and liberates the free base, a decomposition more readily effected by dilute sodium hydroxide or carbonate solution, or by the action of metallic zinc on the alcoholic solution. (2) A small quantity of *p*-benzylaminophenol hydrochloride,



which crystallises from water in long, glassy prisms containing  $\text{H}_2\text{O}$ , and melts in its water of crystallisation at 130° and afterwards at 172°; it is soluble in alcohol or acetic acid. The free base,



separates from alcohol or water in nacreous laminae melting at 89—90° and dissolves in benzene or chloroform.

The interaction of *o*-aminophenol and benzyl chloride yields: (1) *o*-dibenzylaminophenol hydrochloride,  $\text{C}_{20}\text{H}_{19}\text{ON} \cdot \text{HCl}$ , which crystallises from water or alcohol in regular octahedra melting at 200—205°; (2) *o*-benzylaminophenol hydrochloride; the free base crystallises from light petroleum in nacreous laminae melting at 81—82°. T. H. P.

**Action of Iodine Chloride on Catechol.** C. LORING JACKSON and M. C. BOSWELL (*Amer. Chem. J.*, 1906, 35, 519—531).—The experiments described were carried out with the object of preparing tetraiodo-*o*-benzoquinone.

By the action of iodine chloride (270 grams) on catechol (30 grams), a dark red mass is produced containing a large quantity of iodine. On removing the iodine by means of potassium iodide solution, a substance, probably octachlorotri-iodopentacatechol,  $\text{C}_{20}\text{H}_{19}\text{O}_{10}\text{Cl}_8\text{I}_3$ , is obtained, which crystallises from dilute alcohol in long, white, silky needles, melts at 224°, and is soluble in ether, benzene, or acetic acid; its diacetyl derivative was prepared. This compound is converted by nitric acid into a dark red substance, which crystallises from toluene in long, bright red needles, becomes darker on drying, owing

probably to loss of toluene of crystallisation, and then melts at  $272^{\circ}$ ; it tends to become light yellow when treated with benzene, light petroleum, or dilute acetic acid.

If the iodine is not removed from the product of the reaction before treatment with sulphur dioxide, trichlorocatechol is produced, which crystallises with  $\text{H}_2\text{O}$  and melts at  $115^{\circ}$  instead of  $104\text{--}105^{\circ}$ , as stated by Cousin (Abstr., 1895, i, 456).

If 30 grams of catechol are treated with 360 grams of iodine chloride, a compound is obtained, probably *heptachloroiodotricatechol*,  $\text{C}_{18}\text{H}_{10}\text{O}_6\text{Cl}_7\text{I}$ , which crystallises from hot dilute alcohol in long, white, silky needles, melts at  $252^{\circ}$ , and is soluble in alcohol or acetic acid; its *diacetyl* derivative was prepared.

If in preparing this compound the reduction with sulphur dioxide is effected before removing the iodine, tetrachlorocatechol (m. p.  $194\text{--}195^{\circ}$ ) is produced, which crystallises with  $\text{H}_2\text{O}$ .

Indications have been obtained that by varying the proportion of iodine chloride another compound may be obtained which melts at  $270^{\circ}$ .

Attempts were made by other methods to prepare tetraiodocatechol or tetraiodo-*o*-quinone, but without success.

E. G.

**Phloroglucinol.** MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 553; from *Collegium*, 1906, 14—15).—Phloroglucinol, when treated in ethereal solution with diazomethane, gives an almost quantitative yield of an enolic ether melting at  $52.5^{\circ}$ , and it is therefore suggested that diazomethane might be a useful reagent for the study of tautomeric modifications. Both resorcinol and pyrogallol give the pine shaving reaction which hitherto has been supposed to be characteristic of phloroglucinol.

P. H.

**Preparation of Dialkylmalonyl-*p*-phenetidines.** AKTIENGESellschaft FÜR ANILIN-FABRIKATION (D.R.-P. 165311).—Dialkylated malonylphenetidines are obtained by the interaction of 2 mols. of phenetidine and 1 mol. of dialkylmalonyl chloride, the former reagent being dissolved in benzene. Clinical experiments have shown that in addition to their antipyretic properties these dialkylmalonyl-*p*-phenetidines have also a saporific action.

*Diethylmalonyl-p-phenetidine*,  $\text{CEt}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ , crystallises from alcohol in white needles melting at  $186^{\circ}$ ; it is sparingly soluble in hot water, but dissolves readily in hot alcohol or benzene.

*Dipropylmalonyl-p-phenetidine*,  $\text{CPr}^a_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ , resembles the preceding compound and melts at  $143^{\circ}$ .

G. T. M.

**Preparation of Aromatic Alcohols and their Ethers by the Electrolytic Reduction of Aromatic Esters.** CARL METTLER (D.R.-P. 166181).—The carboxyl group of an aromatic ester can be reduced electrolytically when the metal chosen for cathode has a high supertension, lead being the best metal for the purpose. It is necessary also to have a solvent which can conduct the electric current, and concentrated sulphuric acid is found convenient since it may be diluted with water, alcohol, or glacial acetic acid; this solvent may,

however, be replaced by an aqueous-alcoholic solution of phosphoric or hydrochloric acid. Under these conditions the alkyl esters of benzoic acid and its derivatives are reduced, yielding a mixture of the corresponding alcohol and its alkyl ether; the proportion of the two products depends on the constitution of the original ester. In alkaline solutions the alcohol alone is produced. These alcohols and their ethers are readily oxidised to the technically important aromatic aldehydes.

Ethyl benzoate when electrolysed in the cathode cell with a current density of 7 amperes per 100 sq. cm. at 20–30° yielded a mixture of benzyl alcohol and benzyl ethyl ether; the solvent in this case was a mixture of dilute sulphuric acid and alcohol. With this solvent and at a temperature of 60–80°, phenyl benzoate gave rise to a mixture of benzyl alcohol and phenyl benzyl ether. Ethyl *m*-bromobenzoate furnished *m*-bromobenzyl ethyl ether and a small amount of *m*-bromobenzyl alcohol. Benzyl benzoate yielded benzyl alcohol and dibenzyl ether.

In presence of aqueous-alcoholic ammonia, ethyl benzoate on electrolysis furnished only benzyl alcohol. G. T. M.

**Benzyl *iso*Valerate.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 165897).—*Benzyl isovalerate*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{CH}_2\text{Ph}$ , is an ester having valuable therapeutic properties, being a sedative which has no harmful effect on the mucous membrane of the stomach. It is prepared by heating together benzyl chloride and sodium *isovalerate* for ten hours at 160° and purified by fractionation under diminished pressure. The ester which has a pleasant odour and boils at 136° under 25 mm. pressure, can also be prepared by the following processes: the interaction of benzyl alcohol and *isovaleryl* chloride either in pyridine-benzene solution or in the presence of concentrated sulphuric or hydrochloric acid; the condensation of benzyl alcohol and carbonyl chloride in quinoline solution and the interaction of the resulting benzyl chlorocarbonate with sodium *isovalerate* at 160°; the direct condensation of *isovaleric* anhydride and benzyl alcohol at 180–200°. G. T. M.

**Unsymmetrical Diphenylethylene Oxide.** AUGUST KLAGES and JOHANNES KESSLER (*Ber.*, 1906, 39, 1753–1756. Compare Abstr., 1905, i, 523; Tiffeneau and Fourneau, Abstr., 1905, i, 523, 591; this vol., i, 20).—as-*Diphenylchlorohydrin* [*diphenylchloromethyl carbinol*],  $\text{OH} \cdot \text{CPh}_2 \cdot \text{CH}_2\text{Cl}$ , obtained by the interaction of magnesium phenyl bromide (3 mols.) and ethyl chloroacetate (1 mol.) with subsequent decomposition of the product by cold water, melts at 66°, and its vapour has an irritating action on the eyes. It reacts with diethylamine at 100° to give a poor yield of *diphenyldiethylaminomethylcarbinol*,  $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{CPh}_2 \cdot \text{OH}$ , which melts at 49°, and a substance which melts at 154–155° and does not contain nitrogen.

as-*Diphenylethylene oxide*,  $\begin{array}{c} \text{CPh}_2 \\ | \\ \text{CH}_2 \end{array} > \text{O}$ , obtained from the chlorohydrin and sodium ethoxide, is a colourless substance which melts at 56°, turns yellow in the air, and slowly becomes resinous; its vapour



has a pungent odour and is volatile in steam. The sodium hydrogen sulphite compound is decomposed by boiling dilute sulphuric acid or potassium carbonate with the formation of diphenylacetaldehyde, of which the *semicarbazone* melts at 160°, the *azine* at 165°, and the *benzoylhydrazone* at 182°.

C. S.

**Further Investigations of the Two Chlorides of *o*-Sulphobenzoic Acid.** PHILIP H. COBB (*Amer. Chem. J.*, 1906, 35, 486—508).—Experiments on the action of hydrochloric acid on organic anhydrides have led to the conclusion that the formation of symmetrical ester chlorides by the action of alcohol on the more fusible chloride of *o*-sulphobenzoic acid is not dependent on the presence of hydrochloric acid. It has been found that the anhydrides of certain dibasic acids do not react with dry hydrogen chloride, whilst those of monobasic acids are easily attacked.

The action of alcohols and alkyloxides on the chlorides has been studied by Bird (*Abstr.*, 1903, i, 822). The product obtained by the action of methyl alcohol on the more fusible chloride melts at 63—64°. The barium salt containing about 28 per cent. of barium which was obtained by Bird from the product formed by boiling either the less fusible or more fusible chloride with 95 per cent. ethyl alcohol is probably a mixture of salts of *o*-sulphobenzoic acid and the ester acid. Sodium ethoxide reacts with both chlorides with formation of diethyl *o*-sulphobenzoate in each case.

By the action of benzene on the chlorides in presence of aluminium chloride, Remsen and Saunders (*Abstr.*, 1895, i, 474) and List and Stein (*Abstr.*, 1898, i, 584) obtained *o*-benzoyldiphenylsulphone together with a product which melts at 162—163° and was regarded as the lactone,  $C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ \text{SO}_2 \end{smallmatrix} O$ . It is now considered probable that this product is not the supposed lactone.

By the action of thionyl chloride on dipotassium *o*-sulphobenzoate, *o*-sulphobenzoic anhydride is obtained together with a small quantity of the salt,  $COCl \cdot C_6H_4 \cdot SO_3K$ , but no *o*-sulphobenzoic chloride could be isolated. By the action of thionyl chloride on the acid potassium salt, the anhydride can be obtained in an 80 per cent. yield.

When the anhydride is heated with phosphorus oxychloride at 125° for fourteen hours, the more fusible chloride is produced.

By the action of magnesium phenyl bromide on the less fusible chloride, the substance  $SO_2Ph \cdot C_6H_4 \cdot CPh_2 \cdot OH$  is obtained, which crystallises from alcohol, melts at 183—184°, and gives a dark red coloration with concentrated nitric and sulphuric acids. The same substance can be obtained by treating *o*-benzoyldiphenylsulphone with magnesium phenyl bromide. Magnesium phenyl bromide reacts with *o*-sulphobenzoic anhydride with formation of the compound melting at 163°, which is obtained by the action of benzene on the less fusible chloride in presence of aluminium chloride.

E. G.

**Preparation of Methylenehippuric Acid.** CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 163238. Compare *Abstr.*, 1904, i, 413).—Hippuric acid reacts with chloromethyl alcohol or the



less volatile fractions containing hydroxymethylene chlorides (Litterscheid, Abstr., 1901, i, 443) to form methylenehippuric acid. There is less formation of resin than when formaldehyde and an acid are employed. C. H. D.

[Crystallographic Measurements of] Derivatives of Phenylcarbamic Acid. F. M. JAEGER (*Zeit. Kryst. Min.*, 1906, 42, 25—33). —Methyl phenylcarbamate crystallises from alcohol in colourless, rectangular leaflets which melt at  $47^{\circ}$  and belong to the bipyramidal class of the rhombic system [ $a:b=1.5952:1$ ]; it has a sp. gr. 1.251 at  $19^{\circ}$ .

Methyl phenylmethylcarbamate separates from alcohol in large, colourless crystals which melt at  $44^{\circ}$  and belong to the bipyramidal class of the rhombic system [ $a:b:c=0.8406:1:0.3320$ ]; sp. gr. 1.296 at  $19^{\circ}$ .

Methyl 4-nitrophenylmethylcarbamate separates from alcohol or benzene in fine needles or large, pale yellow, somewhat flattened crystals which melt at  $108^{\circ}$  and belong to the prismatic class of the monoclinic system [ $a:b=0.6640:1$ ;  $\beta=70^{\circ}58'$ ]; sp. gr. 1.522 at  $14^{\circ}$ .

Methyl 2:4-dinitrophenylmethylcarbamate crystallises from xylene in pale yellow, parallelogramatic plates, which melt at  $98^{\circ}$  and belong to the prismatic class of the monoclinic system

$$[a:b:c=0.7597:1:1.0875; \beta=88^{\circ}43\frac{1}{3}'];$$

sp. gr. is 1.506 at  $14^{\circ}$ .

Methyl 2:4:6-trinitrophenylcarbamate melts at  $118^{\circ}$  and is dimorphous. The  $\alpha$ -modification is the one usually separating from solvents and is deposited from acetone in very shiny, colourless or pale yellow crystals belonging to the prismatic class of the monoclinic system [ $a:b:c=0.5758:1:0.8382$ ;  $\beta=75^{\circ}41'$ ]; sp. gr. 1.612 at  $19^{\circ}$ . The  $\beta$ -modification occasionally separates from alcohol, along with the  $\alpha$ -form, in long, orange needles which turn yellow at about  $105^{\circ}$  and melt somewhat below  $118^{\circ}$ ; these crystals belong to the bipyramidal division of the rhombic system [ $a:b=0.6596:1$ ]; sp. gr. at  $19^{\circ}$  is 1.601.

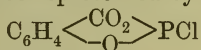
Ethyl 2:4-dinitrophenylmethylcarbamate is deposited from a mixture of benzene and light petroleum in large, colourless, shining crystals, which melt at  $112^{\circ}$  and belong to the prismatic division of the monoclinic system [ $a:b:c=0.6525:1:0.7035$ ;  $\beta=69^{\circ}59'$ ]; sp. gr. 1.461 at  $19^{\circ}$ .

Ethyl 2:4:6-trinitrophenylmethylcarbamate crystallises from a mixture of benzene and light petroleum in slender, transparent, pale yellow needles, which melt at  $65^{\circ}$  and belong to the prismatic division of the monoclinic system [ $a:b:c=0.9759:1:0.3929$ ;  $\beta=67^{\circ}7'$ ]; sp. gr. at  $14^{\circ}$ , 1.471.

2:4:6-Trinitrophenylnitromethylamine crystallises from a mixture of benzene and acetone in small, highly refractive, pale yellow needles, which melt at  $127^{\circ}$  and belong to the prismatic class of the monoclinic system [ $a:b:c=2.7823:1:3.5242$ ;  $\beta=75^{\circ}31\frac{1}{2}'$ ]; sp. gr. at  $19^{\circ}$ , 1.570. T. H. P.

Action of Phosphorus Pentachloride and Trichloride on Substituted *o*-Phenolcarboxylic Acids. RICHARD ANSCHÜTZ (*Annalen*, 1906, 346, 286—300. Compare Anschütz and Emery, Abstr., 1887, 946; Anschütz and Moore, Abstr., 1887, 947; Couper,

*Compt. rend.*, 1858, 46, 1107).—The author discusses the constitution of salicylphosphorous chloride formed by the action of phosphorus trichloride, and of chlorocarboxyphenyl dichloro-orthophosphate formed by the action of phosphorus pentachloride on salicylic acid, and concludes that they must be represented by the formulæ



and  $\text{COCl} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{POCl}_2$  respectively.

Chlorocarboxyphenyl dichloro-orthophosphate, prepared by the action of phosphorus pentachloride on salicylic acid, is identical with the products of the action of chlorine and of phosphorus pentachloride on salicylphosphorous chloride, as when heated with anhydrous oxalic acid at 75—85° all three preparations yield *o*-chlorocarboxyphenyl metaphosphate (Anschütz and Moore, *loc. cit.*), which crystallises from a mixture of benzene and light petroleum, melts at 95°, and boils at 170—171° under 11 mm. pressure.

The *additive* compound, formed by the action of bromine on salicylphosphorous chloride, distils at 185—190° and is a mixture of the compounds  $\text{COBr} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{POClBr}$  and  $\text{COCl} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{POBr}_2$ , as when heated with anhydrous oxalic acid at 85—100° it yields hydrogen chloride and bromide, carbon monoxide and dioxide, and an almost molecular mixture of the compounds  $\text{C}_7\text{H}_4\text{O}_4\text{ClP}$  and  $\text{C}_7\text{H}_4\text{O}_4\text{BrP}$ , which melts at 96—98° and boils at 205—210°, or after repeated distillation at 178—182° under 11 mm. pressure. G. Y.

**Action of Phosphorus Pentachloride and Trichloride on 3:5-Dichlorosalicylic Acid.** RICHARD ANSCHÜTZ and HEINRICH MEHRING (*Annalen*, 1906, 346, 300—311. Compare preceding abstract).—3:5-Dichlorosalicylic acid forms transparent, rhombic crystals [ $a:b:c=0.9983:1:1.2312$ ] and melts at 219° (214°: Smith, *Abstr.*, 1878, 879). The *chloride*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{COCl}$ , formed by heating the acid with 1 mol. of phosphorus pentachloride at 60°, crystallises from a mixture of ether and light petroleum, melts at 79°, and is hydrolysed slowly by moist air, quickly by hot water. The methyl ester, which melts at 147° (143°: Smith, *loc. cit.*) and boils at 160°, and the ethyl ester, which forms rhombic crystals [ $a:b:c=0.9403:1:0.4273$ ], melts at 57° (47°: Smith, *loc. cit.*) and boils at 159° under 11.5 mm. pressure, are prepared by the action of methyl and ethyl alcohols respectively on the acid chloride. The *phenyl ester*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO}_2\text{Ph}$ , crystallises in transparent, rhombic plates [ $a:b:c=0.72877:1:1$ ], melts at 118.5°, and decomposes at 139° under 14 mm. pressure, forming phenol and poly-3:5-dichlorosalicylide. The *anilide*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{NHPh}$ , forms sheaves of transparent crystals, which effloresce when exposed to air, and melts at 134.5°. The *piperidide*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{C}_5\text{H}_{10}\text{N}$ , crystallises in asymmetric plates [ $a:b:c=0.6707:1:0.660$ ] and melts at 108°. The *anhydride*,  $\text{O}(\text{CO} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{OH})_2$ , formed by boiling the acid chloride with the silver salt suspended in ether, crystallises from chloroform, melts at 186—187°, and is only sparingly soluble in water. The *silver*,  $\text{C}_7\text{H}_3\text{O}_3\text{Cl}_2\text{Ag}$ , and *ammonium*,  $\text{C}_7\text{H}_7\text{O}_3\text{NCl}_2$ , salts were analysed.

4:6-Dichloro-2-trichloromethylphenyl dichloro-orthophosphate,  
 $\text{CCl}_3 \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{O} \cdot \text{POCl}_2$ ,

is prepared by heating 3:5-dichlorosalicylic chloride with 1 mol. of phosphorus pentachloride in a sealed tube at 50—60° for twelve hours; it separates from acetone in transparent crystals, which become opaque on exposure to air, melts at 102—104°, is hydrolysed to 3:5-dichlorosalicylic acid when boiled with water for some hours, and, when heated with 1 mol. of phosphorus pentachloride in a sealed tube at 200° yields a mixture of products boiling at 160—190° under 17 mm. pressure; of these, the main product is probably 2:3:5-trichlorobenzotrichloride.

*Poly-3:5-dichlorosalicylide*,  $(\text{O}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO})_x$ , formed when phenyl 3:5-dichlorosalicylate or 3:5-dichlorosalicylic chloride is distilled under reduced pressure, separates from chloroform in white crystals, becomes blackish-brown at 250°, does not melt at 300°, and remains unaltered when boiled with water.

3:5-Dichlorosalicylphosphorous chloride,  $\text{C}_6\text{H}_2\text{Cl}_2\langle\text{CO}_2\rangle\text{PCl}$ , prepared by boiling 3:5-dichlorosalicylic acid with phosphorus trichloride in xylene solution in a reflux apparatus, melts at 55°, boils at 159° under 11 mm. pressure, forms an *additive* compound with chlorine, and is hydrolysed readily by water, forming 3:5-dichlorosalicylic acid.

G. Y.

**Action of Phosphorus Pentachloride and Trichloride on 3-Chlorosalicylic Acid.** RICHARD ANSCHÜTZ and RICHARD ANSPACH (*Annalen*, 1906, 346, 312—317. Compare preceding abstracts).—3-Chlorosalicylic acid melts at 180° (178°: Varnholt, Abstr., 1887, 945). 3-Chlorosalicylic chloride,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{COCl}$ , prepared by boiling the acid with phosphorus pentachloride in light petroleum solution in a reflux apparatus, crystallises in long, white needles, melts at 62—63°, and is readily soluble in ether, glacial acetic acid, benzene, chloroform, and carbon tetrachloride. The methyl ester, prepared by the action of methyl alcohol, melts at 38° (83°: Varnholt, *loc. cit.*); the *ethyl ester*,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{Et}$ , crystallises from alcohol in long, flat needles and melts at 21°, forming a strongly refractive oil with an aromatic odour, which boils at 147° under 12 mm. or at 269—270° under the ordinary pressure. The *anilide*,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}\cdot\text{NHPh}$ , crystallises from alcohol in white, silvery needles and melts at 158·5—159°.

3-Chlorosalicylide and poly-3-chlorosalicylide are formed together with hydrogen chloride when 3-chlorosalicylic chloride is heated about 100° under greatly reduced pressure.

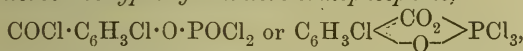
3-Chlorosalicylide,  $\text{C}_6\text{H}_3\text{Cl}\langle\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}\cdot\text{O}\rangle\text{C}_6\text{H}_3\text{Cl}$ ? (compare Anschütz, Abstr., 1893, i, 165), is obtained as a white, voluminous powder, melts at 206°, and is readily soluble in chloroform.

*Poly-3-chlorosalicylide*,  $(\text{C}_7\text{H}_3\text{O}_2\text{Cl})_x$ , separates from xylene as a hard crust, melts at about 330°, and is insoluble in chloroform.

3-Chlorosalicylphosphorous chloride,  $\text{C}_6\text{H}_3\text{Cl}\langle\text{CO}_2\rangle\text{PCl}$ , prepared by heating 3-chlorosalicylic acid with phosphorus trichloride in a reflux apparatus, melts at about 65°, boils at 150° under 12·5 mm.



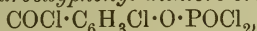
pressure, and when heated with phosphorus pentachloride yields 6-chloro-2-chlorocarboxyphenyl dichloro-orthophosphate,



which boils at 195—196° under 13 mm. pressure and is readily hydrolysed by water. G. Y.

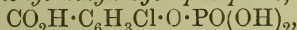
**Action of Phosphorus Pentachloride and Trichloride on 5-Chlorosalicylic Acid.** RICHARD ANSCHÜTZ and RICHARD ANSPACH (*Annalen*, 1906, 346, 318—323. Compare preceding abstracts).—

5-Chlorosalicylphosphorous chloride,  $\text{C}_6\text{H}_3\text{Cl} \left\langle \begin{array}{c} \text{CO}_2 \\ \text{O} \end{array} \right\rangle \text{PCl}$ , formed by the action of phosphorus trichloride on 5-chlorosalicylic acid, melts at 55—57°, boils at 155—156° under 14 mm. pressure, is very sensitive to water, and when treated with phosphorus pentachloride at 105—115° yields 4-chloro-2-chlorocarboxyphenyl dichloro-orthophosphate,



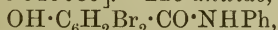
which is formed also by the action of phosphorus pentachloride on 5-chlorosalicylic acid in light petroleum solution. It is obtained as a colourless, strongly refracting oil, which boils at 183—184° under 13 mm. pressure and is easily hydrolysed by moisture.

4-Chloro-2-carboxyphenyl dihydrogen phosphate,



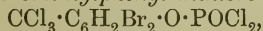
is formed by the action of water on the preceding substance in ethereal solution as a snow-white powder which melts at 161—162°, is hydrolysed to 5-chlorosalicylic acid when boiled with water, and when heated with 1 mol. of phosphorus pentachloride in a sealed tube at 185—190° yields 4-chloro-2-trichloromethylphenyl dichloro-orthophosphate,  $\text{CCl}_3 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{O} \cdot \text{POCl}_2$ . This melts at 59—60°, boils at 197° under 15 mm. pressure, and when heated with 1 mol. of phosphorus pentachloride in a sealed tube at 210—220° forms 2:5-dichlorobenzo-trichloride,  $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{CCl}_3$ , which boils at 150° under 13 mm. pressure, and on prolonged boiling with water in a reflux apparatus is hydrolysed, forming 2:5-dichlorobenzoic acid. G. Y.

**Action of Phosphorus Pentachloride and Trichloride on 3:5-Dibromosalicylic Acid.** RICHARD ANSCHÜTZ and ALFRED ROBITSEK (*Annalen*, 1906, 346, 323—329. Compare preceding abstracts).—3:5-Dibromosalicylic chloride,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{COCl}$ , prepared by heating 3:5-dibromosalicylic acid with phosphorus pentachloride in light petroleum solution or in a sealed tube at 100°, forms hard, yellow, crystalline aggregates, melts at 86.5°, and when boiled with water yields 3:5-dibromosalicylic acid. The ethyl ester prepared by the action of alcohol on the acid chloride is identical with Freer's ester (*Abstr.*, 1893, i, 66); it crystallises in glistening, rhombic plates [ $a:b:c = 0.928715:1:0.519089$ ]. The anilide,



crystallises from alcohol in glistening needles and melts at 139—140°.

4:6-Dibromo-2-trichloromethylphenyl dichloro-orthophosphate,



formed by heating 3:5-dibromosalicylic acid with 2 mols., or the acid



chloride with 1 mol., of phosphorus pentachloride in a sealed tube at 100°, crystallises in large, colourless plates and melts at 129—130°.

3:5-Dibromosalicylide,  $(C_7H_2O_2Br_2)_4$ , is prepared by slowly heating 3:5-dibromosalicylic chloride above its melting point under 12 mm. pressure; it separates from a mixture of chloroform and alcohol as a white, flocculent mass, becomes vitreous at 220°, melts at 230°, and when slowly heated resolidifies at 245—260°, forming a *poly*-3:5-dibromosalicylide,  $(C_7H_2O_2Br_2)_x$ , which is obtained as a white powder, melts and decomposes above 285°, is only sparingly soluble in xylene, is insoluble in other organic solvents or aqueous alkali hydroxides, and is not identical with the *isomerisation product* formed slowly from dibromosalicylide at the ordinary temperature.

3:5-Dibromosalicylphosphorous chloride,  $C_6H_2Br_2\langle\begin{smallmatrix} CO_2 \\ O \end{smallmatrix}\rangle PCl$ , melts at 75—76°, boils at 210° under 12 mm. pressure, forms an *additive* compound with chlorine, fumes in contact with air, and reacts violently with water, being hydrolysed to 3:5-dibromosalicylic acid.

G. Y.

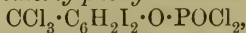
**Action of Phosphorus Pentachloride and Trichloride on 3:5-Di-iodosalicylic Acid.** RICHARD ANSCHÜTZ, ALFRED ROBITSEK, and FRITZ SCHMITZ (*Annalen*, 1906, 346, 330—335. Compare preceding abstracts).—3:5-Di-iodosalicylic chloride,  $OH\cdot C_6H_2I_2\cdot COCl$ , is prepared by heating 3:5-di-iodosalicylic acid with 1 mol. of phosphorus pentachloride in benzene solution at 60°; it forms yellow, crystalline, nodular aggregates, melts at 97—98°, does not react with phosphorus oxychloride at 100°, and is hydrolysed rapidly when heated with water.

The *methyl ester*,  $OH\cdot C_6H_2I_2\cdot CO_2Me$ , formed by the action of methyl alcohol on the acid chloride, melts at 110° and boils and decomposes partially at 221° under 17 mm. pressure. The *ethyl ester*,  $C_9H_8O_3I_2$ , crystallises in glistening, rhombic leaflets, melts at 133°, and decomposes above 200° when heated under reduced pressure. The *anilide*,  $OH\cdot C_6H_2I_2\cdot CO\cdot NHPh$ , melts and decomposes at 173·5°.

When heated above its melting point under 15 mm. pressure, 3:5-di-iodosalicylic chloride forms two di-iodosalicylides.  $\alpha$ -3:5-Di-iodosalicylide,  $(C_7H_2O_2I_2)_x$ , separates from a mixture of chloroform and alcohol as a white, flocculent mass, becomes vitreous at 120°, melts at about 145°, is readily soluble in chloroform or xylene, and decomposes liberating iodine when exposed to light.

$\beta$ -3:5-Di-iodosalicylide,  $(C_7H_2O_2I_2)_x$ , formed chiefly at 150°, crystallises from xylene as a white crust, melts at 101°, and is insoluble in chloroform.

4:6-Di-iodo-2-trichloromethylphenyl dichloro-orthophosphate,



prepared by heating 3:5-di-iodosalicylic acid with 2 mols. of phosphorus pentachloride in a sealed tube at 100° for ten hours, crystallises from light petroleum in large, stellate aggregates, melts at 126°, and is hydrolysed to 3:5-di-iodosalicylic acid when boiled with water.

3:5-Di-iodosalicylphosphorous chloride,  $C_6H_2I_2\langle\begin{smallmatrix} CO_2 \\ O \end{smallmatrix}\rangle PCl$ , formed by heating 3:5-di-iodosalicylic acid with an excess of phosphorus

trichloride, melts at  $126^{\circ}$ , decomposes when heated under reduced pressure, and is hydrolysed readily by water. G. Y.

**Action of Phosphorus Pentachloride and Trichloride on Nitro- and Halogen-nitro-salicylic Acids.** RICHARD ANSCHÜTZ, EVERHARD WEBER, JULIUS SIEBEN, and RICHARD ANSPACH (*Annalen*, 1906, **346**, 336—340. Compare preceding abstracts).—3:5-Dinitrosalicylic chloride,  $\text{OH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{COCl}$ , is prepared by the action of phosphorus pentachloride on 3:5-dinitrosalicylic acid in light petroleum solution; it crystallises from a mixture of benzene and light petroleum in small, thin needles, melts at  $69\text{--}70^{\circ}$ , and reacts with methyl and ethyl alcohols, forming the esters which melt at  $125^{\circ}$  and  $98^{\circ}$  respectively (Cahours, *Annalen*, 1849, **69**, 230, 235), and are formed also by the action of methyl and ethyl alcohols on the products of the reaction of the acid chloride with methyl and ethyl sodiomalonates. When heated to  $70\text{--}80^{\circ}$ , the acid chloride evolves hydrogen chloride and yields an impure 3:5-dinitrosalicylide,  $(\text{C}_7\text{H}_2\text{O}_6\text{N}_2)_x$ , which is obtained as a greyish-yellow powder, melts at  $150\text{--}155^{\circ}$ , is hydrolysed by cold water forming 3:5-dinitrosalicylic acid, and when treated with ethyl alcohol in chloroform solution forms ethyl 3:5-dinitrosalicylate.

3-Nitrosalicylic chloride,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{COCl}$ , formed in the same manner as the 3:5-dinitro-acid chloride, crystallises from a mixture of benzene and light petroleum in sheaves of large, long plates, melts at  $59\text{--}61^{\circ}$ , and is hydrolysed to 3-nitrosalicylic acid when boiled with water.

5-Chloro-3-nitrosalicylic chloride,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)\cdot\text{COCl}$ , formed from 5-chloro-3-nitrosalicylic acid melting at  $163^{\circ}$ , could not be purified from phosphorus pentachloride; when treated with alcohol, it yields the ethyl ester, melting at  $90\text{--}91^{\circ}$ .

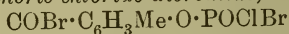
5-Bromo-3-nitrosalicylic chloride,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{COCl}$ , separates from a mixture of benzene and light petroleum in stout, yellow crystals and melts at  $56\cdot5^{\circ}$ .

3-Bromo-5-nitrosalicylic chloride,  $\text{C}_7\text{H}_3\text{O}_4\text{NClBr}$ , forms stout, white crystals and melts at  $95\text{--}96^{\circ}$ . G. Y.

**Action of Phosphorus Pentachloride and Trichloride on  $\beta$ -Cresotic Acid [2-Hydroxy-*m*-toluic Acid; 3-Methylsalicylic Acid].** RICHARD ANSCHÜTZ, ERNST SCHROEDER, EVERHARD WEBER, and RICHARD ANSPACH (*Annalen*, 1906, **346**, 341—349. Compare preceding abstracts).—2-Hydroxy-*m*-toluoyl chloride,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{COCl}$ , prepared by the action of phosphorus pentachloride on 2-hydroxy-*m*-toluic acid in light petroleum solution, solidifies in a freezing mixture and melts at  $27\text{--}28^{\circ}$ . Silver 2-hydroxy-*m*-toluate,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{Ag}$ , forms a white, granular powder, which blackens slowly on exposure to light. The amide,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{NH}_2$ , crystallises from dilute alcohol in small, dull, white needles and melts at  $112^{\circ}$ ; the anilide,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{NHPh}$ , crystallises in sheaves of needles and melts at  $123^{\circ}$ ; the piperidide,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{C}_5\text{H}_{10}\text{N}$ , forms monoclinic plates [ $a:b:c = 1\cdot34217:1:1\cdot88072$ ;  $\beta = 77^{\circ}29\cdot5'$ ] and melts at  $53^{\circ}$ .

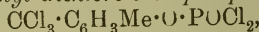
3-Methylsalicylphosphorous chloride,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{PCl}$ , prepared by boiling 2-hydroxy-*m*-toluic acid with phosphorus trichloride in xylene solution in a reflux apparatus, melts at  $36\text{--}37^\circ$ , boils at  $143.6\text{--}144^\circ$  under 14 mm. pressure, and when heated with phosphorus pentachloride forms 3-chlorocarboxy-*o*-tolyl dichloro-orthophosphate,  $\text{COCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{POCl}_2$ , which is formed also by the action of chlorine on the fused phosphorous chloride. It is obtained as a transparent liquid, which boils at  $185.6\text{--}186.2^\circ$  under 12 mm. pressure and is hydrolysed by moisture.

3-Methylsalicylphosphoric chloride dibromide,

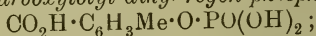


or  $\text{COCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{POBr}_2$ , prepared by the action of bromine on the phosphorous chloride, is obtained as a transparent oil which boils at  $200\text{--}202^\circ$  under 15 mm. pressure, is very unstable, and forms 2-hydroxy-*m*-toluic acid when boiled with aqueous sodium hydroxide.

3-Trichloromethyl-*o*-tolyl dichloro-orthophosphate,



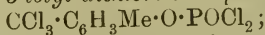
prepared by boiling 2-hydroxy-*m*-toluic acid with 2 mols. of phosphorus pentachloride in carbon tetrachloride solution in a reflux apparatus, crystallises in prismatic plates, melts at  $80^\circ$ , boils at  $199.4\text{--}199.8^\circ$  under 13 mm. pressure, and is hydrolysed readily by water in ethereal solution, forming 3-carboxytolyl dihydrogen phosphate,



this is a white, crystalline substance and melts at  $148\text{--}149^\circ$ .

G. Y.

Action of Phosphorus Pentachloride and Trichloride on *m*-Cresotic Acid (3-Hydroxy-*p*-toluic Acid; 4-Methylsalicylic Acid). RICHARD ANSCHÜTZ and ERNST SCHROEDER (*Annalen*, 1906, 346, 349—353. Compare preceding abstracts).—4-Chlorocarboxy-3-tolyl dichloro-orthophosphate,  $\text{COCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{POCl}_2$ , formed by the action of phosphorus pentachloride on 3-hydroxy-*p*-toluic acid or by the action of chlorine or phosphorus pentachloride on 4-methylsalicylphosphorous chloride, is obtained as a clear, strongly refracting, viscid liquid, which boils at  $184.6\text{--}185.4^\circ$  under 12 mm. pressure, and, when heated with phosphorus pentachloride in a sealed tube at  $165\text{--}170^\circ$ , yields 4-trichloromethyl-3-tolyl dichloro-orthophosphate,



this could not be purified from accompanying substitution products.

4-Chlorocarboxy-3-tolyl metaphosphate,  $\text{COCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{PO}_2$ , prepared by carefully heating the dichloro-orthophosphate with anhydrous oxalic acid and distilling the product under reduced pressure, crystallises in long plates, melts at about  $77^\circ$ , and boils at  $195.4\text{--}196.2^\circ$  under 14 mm. pressure.

4-Carboxy-3-tolyl dihydrogen phosphate,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{PO}(\text{OH})_2$ , formed by the action of water on the dichloro-orthophosphate, melts at  $150^\circ$ .

4-Methylsalicylphosphorous chloride,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{PCl}$ , prepared by heating 3-hydroxy-*p*-toluic acid with phosphorus trichloride in xylene



solution in a reflux apparatus, forms a white, crystalline mass, melts at  $45^{\circ}$ , and boils at  $150\text{--}151^{\circ}$  under 13 mm. pressure.

4-Methylsalicylphosphoric chloride dibromide,  $\text{COCl}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POBr}_2$  or  $\text{COBr}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POClBr}$ , prepared by the action of bromine on 4-methylsalicylphosphorous chloride, is obtained as a clear, viscid liquid, which soon becomes yellow, boils at  $202\text{--}203^{\circ}$  under 13 mm. pressure, and is readily hydrolysed by moisture. G. Y.

Action of Phosphorus Pentachloride and Trichloride on *p*-Cresotic Acid (5-Methylsalicylic Acid; 4-Hydroxy-*m*-toluic Acid). RICHARD ANSCHÜTZ and ERNST SCHROEDER (*Annalen*, 1906, 346, 354—357. Compare preceding abstracts).—2-Chlorocarboxy-*p*-tolyl dichloro-orthophosphate,  $\text{COCl}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POCl}_2$ , formed by the action of phosphorus pentachloride on 4-hydroxy-*m*-toluic acid or of phosphorus pentachloride or chlorine on 5-methylsalicylphosphorous chloride, is obtained as a transparent, strongly refracting liquid, which boils at  $185^{\circ}$  under 12 mm. pressure, yields 4-hydroxy-*m*-toluic acid when boiled with water, and when heated with phosphorus pentachloride in a sealed tube at  $165\text{--}170^{\circ}$  forms a mixture of products boiling at  $183\text{--}225^{\circ}$  under 13 mm. pressure.

2-Chlorocarboxy-*p*-tolyl metaphosphate,  $\text{COCl}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{PO}_2$ , formed by the action of anhydrous oxalic acid or the dichloro-orthophosphate, crystallises from ether in plates, melts at  $88^{\circ}$ , and boils at  $185\text{--}186^{\circ}$  under 14 mm. pressure.

2-Carboxy-*p*-tolyl dihydrogen phosphate,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{PO}(\text{OH})_2$ , forms a white, crystalline mass and melts at  $139\cdot5\text{--}140\cdot4^{\circ}$ .

5-Methylsalicylphosphorous chloride,  $\text{C}_6\text{H}_3\text{Me}\langle\text{CO}_2\rangle\text{PCl}$ , melts at  $61^{\circ}$ , boils at  $145\cdot6\text{--}146\cdot4^{\circ}$  under 12 mm. pressure, and reacts with bromine forming 5-methylsalicylphosphoric chloride dibromide,  $\text{COCl}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POBr}_2$  or  $\text{COBr}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{POClBr}$ , which solidifies in a freezing mixture and melts in the hand to a transparent oil boiling at  $205\text{--}207^{\circ}$  under 15 mm. pressure; it is easily hydrolysed by water. G. Y.

Action of Phosphorus Pentachloride and Trichloride on 2-Hydroxyuvitic Acid. RICHARD ANSCHÜTZ and ALFRED ROBITSEK (*Annalen*, 1906, 346, 357—360. Compare preceding abstracts).—2-Hydroxyuvityl dichloride,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}(\text{COCl})_2[\text{OH}:\text{Me}:\text{COCl}:\text{COCl}=2:3:1:5]$ , prepared by the action of phosphorus pentachloride on 2-hydroxyuvitic acid in light petroleum solution, crystallises in sheaves of colourless needles, melts at  $67\text{--}68^{\circ}$ , decomposes when distilled under reduced pressure, is moderately stable when exposed to air, and is hydrolysed when heated with water. The dimethyl ester, formed by the action of methyl alcohol on the dichloride, melts at  $132^{\circ}$  ( $128^{\circ}$ : Jacobsen, *Abstr.*, 1881, 431); the diethyl ester,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}(\text{CO}_2\text{Et})_2$ , crystallises from light petroleum in colourless needles and melts at  $62^{\circ}$ . The dianilide,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}(\text{CO}\cdot\text{NHPh})_2$ , crystallises in transparent prisms which soon become opaque and melts at  $238^{\circ}$ .

The action of phosphorus trichloride on 2-hydroxyuvitic acid leads to the formation of an extremely hygroscopic, colourless, viscid oil, which reacts energetically with water, forming 2-hydroxyuvitic acid. G. Y.



**Action of Phosphorus Pentachloride on 1-Hydroxy-2-Naphthoic Acid.** RICHARD ANSCHÜTZ, EVERHARD WEBER, and KARL RUNKEL (*Annalen*, 1906, **346**, 360—381. Compare preceding abstracts; Wolffenstein, *Abstr.*, 1887, 963; 1888, 714).—After purification by conversion into the ammonium salt and precipitation by hydrochloric acid, 1-hydroxy-2-naphthoic acid melts at 191—192° (187°: Schmidt and Burkhardt, *Abstr.*, 1888, 59). 1-Hydroxy-2-naphthoyl chloride,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{COCl}$ , formed by the action of phosphorus pentachloride on the acid in light petroleum solution, crystallises in long, yellow needles, melts at 85—86°, and when treated with ammonia in ethereal solution yields the *amide*  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NH}_2$ , which forms yellow, granular crystals and melts at 202°. The *anilide*,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NHPh}$ , forms white, glistening crystals and melts at 154°.

The chief part of this paper consists of a *résumé* and discussion of the results described in this and the preceding papers. G. Y.

**3 : 6-Dibromo-2'-dimethylaminobenzoylbenzoic Acid, the Corresponding Diethyl Compound, and their Derivatives.** ÉMILE SÉVERIN (*Compt. rend.*, 1906, **142**, 1274—1276. Compare *Abstr.*, 1900, i, 296, 450, 598).—3 : 6-Dibromo-2'-dimethylaminobenzoylbenzoic acid,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CO}_2\text{H}$ , prepared by Haller and Guyot's method (compare *Abstr.*, 1894, i, 602) from 1 : 4-dibromophthalic acid (Guareschi, *Abstr.*, 1888, 1300), crystallises from alcohol in magnificent citron-yellow plates and melts at 249°; the *acetate* (mixed anhydride) crystallises from benzene and alcohol in brilliant plates and melts at 195°; the *methyl* ester prepared by the action of sodium methoxide on the acetate forms white, highly refractive crystals which melt at 180°; the *ethyl* ester, similarly prepared, melts at 173°; the *nitroso*-derivative  $\text{NO}\cdot\text{NMe}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CO}_2\text{H}$ , prepared by the action of sodium nitrite on the original acid, forms pale yellow needles which melt at 165°.

3 : 6-Dibromo-2'-dimethylaminobenzoylbenzoic acid,  
 $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CO}_2\text{H}$ ,  
 obtained by reducing the corresponding benzoylbenzoic acid, crystallises with difficulty, melts at 253°, and is converted into 1-dimethylamino-5 : 8-dibromoanthraquinone,  $\text{C}_6\text{H}_2\text{Br}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NMe}_2$ , by the prolonged action of concentrated sulphuric acid at 66°; this compound forms bronze-red needles and melts at 218°.

3 : 6-Dibromo-2'-diethylaminobenzoylbenzoic acid,  
 $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CO}_2\text{H}$ ,  
 forms yellow plates and melts at 221°; the *acetate* forms white plates and melts at 159°, and the *methyl* ester forms refractive crystals and melts at 186°. M. A. W.

**Formation of Unsaturated Ketolactones from  $\alpha\beta$  Diacylcarboxylic Esters.** WALTHER BORSCHKE and ALBERT FELS (*Ber.*, 1906, **39**, 1809—1818).—Ethyl acetophenoneacetoacetate (Paal, *Abstr.*, 1883, 598) is quantitatively obtained from ethyl sodioacetoacetate and  $\omega$ -bromoacetophenone in ethereal solution. When heated with sodium ethoxide, or when distilled, the ester yields Paal's dehydroacetophenone-acetone-

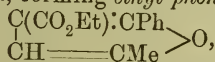
carboxylic acid (Abstr., 1885, 248), which, from its general behaviour and from its resemblance to Knorr's acetylangelicalactone (Abstr., 1899, i, 194; compare also Abstr., 1889, 384; 1897, i, 63), the author concludes to be the lactone of  $\gamma$ -hydroxy- $\alpha$ -acetyl- $\gamma$ -phenyl- $\Delta^{\beta}$ -butenoic acid,

$\begin{array}{c} \text{CHAc} \cdot \text{CO} \\ | \\ \text{CH} = \text{CPh} \end{array} > \text{O}$ . It reduces ammoniacal silver solutions, is soluble

in alkali carbonates, develops a greenish-blue coloration with ferric chloride, and is reconverted into the parent substance by boiling alcohol. By benzylation in pyridine, a *benzoate* is obtained, which separates from alcohol in long, rose-red needles, melts at  $160$ — $161^{\circ}$ , and is converted by phenylhydrazine in alcoholic solution into the *phenylhydrazone* of the original lactone, which crystallises in golden-yellow needles and melts at  $168^{\circ}$ . The *semicarbazone* melts and decomposes at  $264^{\circ}$ .

C. S.

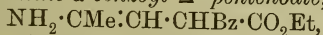
**Synthetical Experiments with Ethyl Benzoylacetonylacetate.** WALTHER BORSCHÉ and ALBERT FELS (*Ber.*, 1906, 39, 1922—1929).—Ethyl benzoylacetonylacetate,  $\text{CH}_2\text{Ac} \cdot \text{CHBz} \cdot \text{CO}_2\text{Et}$ , is prepared by heating ethyl sodiobenzoylacetate with iodoacetone in alcoholic solution; it is obtained as a dark-coloured, heavy oil, which decomposes when distilled, forming *ethyl phenuvate*,



which distils at  $193$ — $194^{\circ}$  under 20 mm. pressure, and on hydrolysis yields phenuvic acid (compare Paal, *Habilitations-schrift*, Würzburg, 1890). On elimination of carbon dioxide, this acid yields 2-phenyl-5-methylfuran.

1-Phenyl- $\Delta^1$ -cyclopentene-3-one,  $\begin{array}{c} \text{CH}_2 \cdot \text{CPh} \\ | \\ \text{CH}_2 - \text{CO} \end{array} > \text{CH}$  is formed together with benzoic and lævulic acids when ethyl benzoylacetonylacetate is boiled with 2 per cent. aqueous sodium hydroxide; it is identical with Paal's dehydrophenacylacetone (Abstr., 1884, 1177). The action of 2 per cent. alcoholic potassium hydroxide on ethyl benzoylacetonylacetate at the ordinary temperature leads to the formation of phenacylacetone, which is isolated as the 4-phenylsemicarbazone,  $\text{C}_{25}\text{H}_{26}\text{O}_2\text{N}_6$ , crystallising in white needles and melting at  $194$ — $195^{\circ}$ . When heated with dilute hydrochloric acid, ethyl benzoylacetonylacetate yields ethyl phenuvate, which is hydrolysed and partially decomposed, yielding 2-phenyl-5-methylfuran, together with a small amount of phenylcyclopentenone.

The action of ammonia on ethyl benzoylacetonylacetate leads to the formation of *ethyl  $\gamma$ -amino- $\alpha$ -benzoyl- $\Delta^{\beta}$ -pentenoate*,

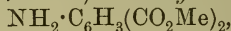


which readily changes into *ethyl 2-phenyl-5-methylpyrrole-3-carboxylate*,  $\text{C}_4\text{NH}_2\text{MePh} \cdot \text{CO}_2\text{Et}$ . The action of aniline on ethyl benzoylacetonylacetate leads to the formation of 1:2-diphenyl-5-methylpyrrole-3-carboxylate,  $\text{C}_4\text{NHMePh}_2 \cdot \text{CO}_2\text{Et}$ , which crystallises in glistening needles and melts at  $133.5^{\circ}$ . The *acid*,  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ , crystallises in glistening, silvery leaflets and melts and decomposes at  $267^{\circ}$ , forming carbon dioxide and 1:2-diphenyl-5-methylpyrrole.

Ethyl benzoylacetonylacetate reacts with semicarbazide in alcoholic solution, forming a *product*,  $C_{15}H_{17}O_3N_3$ , which crystallises in white needles, melts at  $224-226^\circ$ , and is readily soluble in hot alcohol, together with a small quantity of the sparingly soluble *semicarbazone* of the ketone,  $C_{14}H_{16}O_3 \cdot N \cdot NH \cdot CO \cdot NH_2$ , which melts at  $255-260^\circ$ .

The *product*,  $C_{28}H_{28}O_2N_4$ , of the condensation of ethyl benzoylacetonylacetate with phenylhydrazine crystallises in glistening needles and melts and decomposes at  $139-140^\circ$ . G. Y.

**Methyl 4-Aminophthalate and Certain of its Acyl Derivatives.** MARSTON T. BOGERT and ROEMER R. RENSHAW (*J. Amer. Chem. Soc.*, 1906, 28, 617—624).—*Methyl 4-aminophthalate*,



obtained by the reduction of methyl 4-nitrophthalate, crystallises in alcohol or benzene in white, lustrous plates, and from water in long, hexagonal prisms, melts at  $84^\circ$  (corr.), and is soluble in alcohol, acetone, or chloroform, and slightly so in hot water, carbon tetrachloride, or ether. The *hydrochloride* forms a crystalline mass.

By the action of glacial formic acid on the ester, the *compound*,  $C_6H_3(CO_2Me)_2 \cdot NH \cdot CH \cdot N \cdot C_6H_3(CO_2Me)_2$ , is obtained, which forms nearly colourless, microscopic crystals, melts at  $179^\circ$  (corr.), and is soluble in alcohol, hot ethyl acetate, acetone, or benzene. *Methyl 4-acetylaminophthalate*,  $NHAc \cdot C_6H_3(CO_2Me)_2$ , obtained by the action of acetic anhydride on the ester, crystallises in small, colourless plates and melts at  $136.5^\circ$  (corr.). The corresponding *propionyl* derivative crystallises in long, thin, colourless needles and melts at  $110.5^\circ$  (corr.). The *isobutyryl* derivative forms long, thin, colourless needles and melts at  $122-123^\circ$  (corr.). The *benzoyl* derivative forms colourless needles and melts at  $132-132.5^\circ$  (corr.). The *m-nitrobenzoyl* derivative crystallises in nearly colourless scales and melts at  $147^\circ$  (corr.). The *p-nitrobenzoyl* derivative crystallises from alcohol in small, yellow flakes and melts at  $202^\circ$  (corr.).

*Methyl 4-urethanophthalate*,  $C_6H_3(CO_2Me)_2 \cdot NH \cdot CO_2Et$ , separates from boiling water in long needles and melts at  $122^\circ$  (corr.). *Methyl 4-phenyluraminophthalate*,  $C_6H_3(CO_2Me)_2 \cdot NH \cdot CO \cdot NHPh$ , forms microscopic needles and melts at  $138^\circ$  (corr.).

*Methyl 4-ethyloxalylaminophthalate*,  $C_6H_3(CO_2Me)_2 \cdot NH \cdot CO \cdot CO_2Et$ , obtained by the action of ethyl oxalate on the ester, crystallises in small, white flakes and melts at  $121.5^\circ$  (corr.). *Methyl oxalyl-4-aminophthalate*,  $C_2O_2[NH \cdot C_6H_3(CO_2Me)_2]_2$ , obtained as a white precipitate in the preparation of the preceding compound, melts at  $239^\circ$  (corr.). The *phthalamic acid*,  $C_6H_3(CO_2Me)_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$ , forms microscopic crystals and melts at  $166-167^\circ$  (corr.); its *silver* salt is described. The corresponding *succinamic acid* crystallises from water in colourless needles, melts at  $173^\circ$  (corr.), and loses water with probable formation of the imide; the *silver* salt is described. 4-

*Aminophthalanil*,  $NH_2 \cdot C_6H_3 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > NPh$ , obtained by boiling methyl 4-aminophthalate with aniline, crystallises in long, yellow needles and melts at  $205.5^\circ$  (corr.). E. G.



**Synthesis of Ethyl Tetrahydroquinonedicarboxylate.**  
 HYPOLYT TREPHILIEFF (*Ber.*, 1906, 39, 1863—1864).—When ethyl sodioacetoacetate (1 mol.) and ethyl  $\gamma$ -bromoacetoacetate react in ethereal solution, a yellow, crystalline substance is obtained, which is Duisberg's ethyl tetrahydroquinonedicarboxylate (*Abstr.*, 1882, 1192).  
 C. S.

**Benzaldehyde Derivatives of Sugars and Glucosides.**  
 WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Rec. trav. chim.*, 1906, 25, 153—161. Compare Lobry de Bruyn and Alberda van Ekenstein, *Abstr.*, 1899, i, 661; 1900, i, 619; 1902, i, 745; and Schiff, *Abstr.*, 1888, 572).—These products are obtained usually by mixing the sugar with benzaldehyde and adding phosphoric oxide gradually with constant stirring. The mixture is set aside for some time and then poured into water, when the condensation product separates usually as a crystalline powder, which is recrystallised from hot methyl alcohol or from chloroform. None of the products reduce Fehling's solution, and all are hydrolysed into their generators by boiling with dilute sulphuric acid.

*Dibenzylidenearabinose*,  $C_7H_6 \begin{matrix} O \cdot CH \cdot O \cdot CH \cdot CH_2 \cdot O \\ O \cdot CH - CH \cdot O - C_7H_6 \end{matrix}$ , melts at  $154^\circ$ , has  $[\alpha]_D + 26.8^\circ$  in methyl alcohol (showing no mutarotation), and is not acted upon by emulsin at  $35^\circ$ . The number of benzylidene groups present may be determined by boiling a solution of the substance with phenylhydrazine and dilute sulphuric acid and weighing the benzaldehydephenylhydrazone formed.

*Dibenzylidenexylose* melts at  $130^\circ$ , has  $[\alpha]_D + 37.5^\circ$ . *Dibenzylidenemannose* melts at  $128^\circ$ , has  $[\alpha]_D + 56.3^\circ$ , and is hydrolysed with difficulty by dilute sulphuric acid.

Amorphous *dibenzylidene* derivatives of dextrose, mannose, galactose, laevulose, and sorbose were obtained, possibly mixed with monobenzylidene derivatives. The crude products react with acetic anhydride, forming *monoacetyl* derivatives. Glucosides condense readily with benzaldehyde when heated with it in presence of anhydrous sodium sulphate. The products do not reduce Fehling's solution, and are hydrolysed by boiling with dilute sulphuric acid.

*Benzylidene- $\alpha$ -methylglucoside* crystallises from boiling water, melts at  $158^\circ$ , and has  $[\alpha]_D + 85^\circ$  in aqueous solution. *Benzylidene- $\beta$ -methylglucoside* melts at  $194^\circ$ , has  $[\alpha]_D - 75^\circ$  in methyl alcohol, and is not acted on by emulsin.  $\alpha$ -Methylmannoside gives rise to both a *mono-* and a *di-benzylidene* derivative. The first melts at  $110^\circ$ , is slightly laevorotatory, and readily soluble in water; the second melts at  $178^\circ$  and has  $[\alpha]_D - 5^\circ$  in chloroform. *Benzylidene- $\alpha$ -methylgalactoside* melts at  $152^\circ$  and has  $[\alpha]_D + 120.7^\circ$  in methyl alcohol.

*Benzylidenesalicin* crystallises from methyl alcohol, melts at  $187^\circ$ , and has  $[\alpha]_D - 48.3^\circ$  in acetone. *Benzylidenearbutin* melts at  $218^\circ$  and has  $[\alpha]_D - 24.2^\circ$  in methyl alcohol.

*Di-p-toluidylidenearabinose*, produced by condensation in presence of phosphoric oxide at the atmospheric temperature, crystallises from methyl alcohol, melts at  $164^\circ$ , and has  $[\alpha]_D + 2.9^\circ$  in chloroform. The corresponding *xylose* derivative melts at  $140^\circ$ , has  $[\alpha]_D + 45.6^\circ$  in



acetone, and is hydrolysed with difficulty by boiling with dilute sulphuric acid. *p-Toluylidene- $\alpha$ -methylglucoside* melts at  $178^\circ$  and has  $[\alpha]_D + 83.2^\circ$  in methyl alcohol. The corresponding *derivative* of methylmannoside is a syrup, and has  $[\alpha]_D + 29.5^\circ$ ; that of  $\alpha$ -methylgalactoside melts at  $146^\circ$  and has  $[\alpha]_D + 142^\circ$  in methyl alcohol, and that of salicin melts at  $144^\circ$  and has  $[\alpha]_D - 16^\circ$  in methyl alcohol.

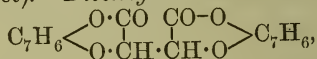
The *product* formed by condensing  $\beta$ -methylglucoside with cumin-aldehyde in presence of anhydrous sodium sulphate, melts at  $124^\circ$  and has  $[\alpha]_D - 34.8^\circ$ .

Salicylaldehyde does not condense with sugars in presence of phosphoric oxide, but reacts readily with glucosides. The  $\alpha$ -methylglucoside *mono-derivative* separates from warm water in colourless crystals, melts at  $182^\circ$  and has  $[\alpha]_D + 91.2^\circ$  in water. The *product* formed with salicin melts at  $163^\circ$  and has  $[\alpha]_D - 32^\circ$  in methyl alcohol.

T. A. H.

### Benzylidene and Toluylidene Derivatives of Hydroxy-acids.

ALBERDA VAN EKENSTEIN and JAN C. I. BLANKSMA (*Rec. trav. chim.*, 1906, 25, 162—164. Compare Alberda van Ekenstein, 1901, i, 120; Lobry de Bruyn and Alberda van Ekenstein, 1899, i, 904; 1902, i, 76, and preceding abstract).—*Dibenzylidene-d-tartaric acid*,



prepared by condensing benzaldehyde with tartaric acid in presence of phosphoric oxide, crystallises from methyl alcohol in long, colourless needles, melts at  $145^\circ$ , has  $[\alpha]_D + 128^\circ$  in methyl alcohol, and is hydrolysed by boiling dilute sulphuric acid. The similar *condensation product* formed with tolualdehyde crystallises from a mixture of light petroleum and benzene, melts at  $177^\circ$ , and has  $[\alpha]_D + 107^\circ$  in methyl alcohol. The *l*-tartaric acid *derivative* melts at  $166^\circ$  and has  $[\alpha]_D - 85.8^\circ$ , and that of racemic acid, which may be obtained from racemic acid or by crystallising together the ditoluylidene derivatives of *d*- and *l*-tartaric acids, melts at  $152^\circ$ .

*Benzylidenecitric acid*,  $\text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2 \begin{array}{c} \diagup \text{CO} \cdot \text{O} \\ \diagdown \text{O} - \text{C}_7\text{H}_6 \end{array}$ , prepared by the general method, crystallises from a mixture of benzene and light petroleum and melts at  $178^\circ$ . The *potassium* and *sodium* salts are amorphous; those of barium and calcium are slightly soluble in water. Saccharic, isosaccharic, and gulonic acids also condense with benzaldehyde in presence of phosphoric oxide.

T. A. H.

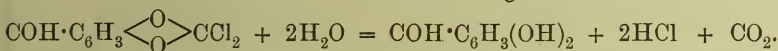
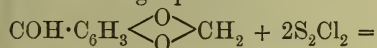
**Sulphonation of 2-Chloro-5-nitrobenzaldehyde with Alkali Sulphites.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 165613).—On boiling 2-chloro-5-nitrobenzaldehyde with aqueous alkali sulphites, sulphonation does occur, but the product is contaminated with a large amount of diazotisable substances. A quantitative yield of 5-nitrobenzaldehyde-2-sulphonic acid is obtained, however, on heating an alcoholic solution of the foregoing aldehyde with sodium sulphite, which remains in suspension in this medium. From the alcoholic filtrate, the sodium salt of the sulphonic acid separates on cooling in yellow crystals.

G. T. M.

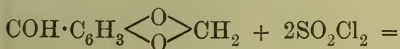
**Preparation of Protocatechualdehyde.** FRANZ FRITZSCHE & Co. (D.R.-P. 162822).—Heliotropin is converted almost quantitatively into protocatechualdehyde by heating at 185—190° under 12 atmospheres pressure with dilute acids or acid metallic salts. The charring which is observed when heliotropin is heated alone at 200° does not take place.

C. H. D.

**Preparation of Protocatechuic Aldehyde from Piperonaldehyde or its Chloride.** SCHIMMEL & Co. (D.R.-P. 165727).—Piperonaldehyde may be converted directly into protocatechuic aldehyde by heating at 130° with sulphur chloride ( $S_2Cl_2$ ) until the evolution of hydrogen chloride has ceased, then boiling with water, filtering the solution from precipitated sulphur, and extracting the required aldehyde with ether. The reactions involved may be expressed by the following equations:



This change may also be effected either with sulphur dichloride ( $SCl_2$ ) or by passing chlorine into a mixture of sulphur and piperonaldehyde. The chlorination stage of the process may also be effected with sulphuryl chloride, in which case the action takes place as follows:



G. T. M.

**2-Chlorocyclohexanone and its Derivatives.** LOUIS BOUVEAULT and F. CHEREAU (*Compt. rend.*, 1906, 142, 1086—1087).—2-Chlorocyclohexanone is obtained by treating cyclohexanone or cyclohexanol in water with chlorine in presence of calcium carbonate. When freshly prepared it is a colourless liquid and boils at 82—83°, but gradually solidifies, forming splendid crystals, and melts at 23°. When boiled with a strong solution of potassium carbonate in water, it passes into 2-hydroxycyclohexanone. This sublimes at 25° under reduced pressure and at 100° under atmospheric pressure, melts at 113° in a closed tube, and is very soluble in warm alcohol, less so in cold, and insoluble in ether or light petroleum. The semicarbazone is colourless and melts at 165°. On oxidation with permanganate, it furnishes adipic acid. Nitric acid converts it into oxalic and succinic acids.

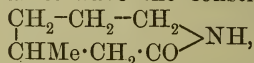
1-Methyl-6-cyclohexanone, prepared from 2-chlorocyclohexanone by the Grignard reaction, boils at 160° under 10 mm. pressure; the semicarbazone melts at 195°. 1-Ethyl-6-cyclohexanone boils at 65° under 10 mm. pressure: its semicarbazone melts at 157°. 1-isoPropyl-6-cyclohexanone boils at 80° under 10 mm. pressure.

T. A. H.

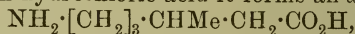
**Terpenes and Ethereal Oils. LXXIX.** Compounds of the *cyclohexanone* Series. OTTO WALLACH (*Annalen*, 1906, 346, 249—265. Compare Sabatier and Mailhe, *Abstr.*, 1905, i, 275).—The properties of 1:2-, 1:4-, and 1:3-methyl*cyclohexanones* are compared. Under the conditions described previously (*Abstr.*, 1900, i, 590), the oxime of 1:2-methyl*cyclohexanone* is converted into the *isooxime*, which crystallises in prisms or needles, melts at 90—91°, and forms an insoluble *hydrochloride*,  $C_{17}H_{13}ON, HCl$ .

1:4-Methyl*cyclohexanone*, prepared by Sabatier and Mailhe's method (*loc. cit.*), boils at 169—171°; it forms a characteristic, yellow *dibenzylidene* derivative,  $CHMe \begin{smallmatrix} \text{CH}_2 \cdot C(CHPh) \\ \text{CH}_2 \cdot C(CHPh) \end{smallmatrix} > CO$ , melting at 98—99°, and an *oxime* melting at 37—39° and boiling at about 114° under 14 mm. pressure. The corresponding *isooxime*, which is very soluble, yields a solid *hydrochloride*,  $C_7H_{13}ON, HCl$ .

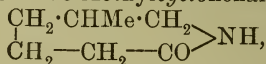
$\alpha$ -*iso*Oxime of 1:3-methyl*cyclohexanone* (*Abstr.*, 1900, i, 590), melting at 104—105°, must have the constitution



as when boiled with hydrochloric acid it forms an *amino-acid*,



which, on oxidation with alkaline permanganate, yields  $\beta$ -methyladipic acid. The  $\beta$ -*isooxime* of 1:3-methyl*cyclohexanone*,



when boiled with hydrochloric acid, yields the *hydrochloride* of the amino-acid,  $CO_2H \cdot [CH_2]_3 \cdot CHMe \cdot CH_2 \cdot NH_2, HCl$ , which, when treated with sodium nitrite and oxidised with chromic acid, forms  $\gamma$ -acetylbutyric acid; the semicarbazone of this melts at 177° (compare *Abstr.*, 1904, i, 752).

The oxime of 3:5:5-trimethyl*cyclohexanone* (*Abstr.*, 1902, i, 806) melts at 84—85° (58°: Knoevenagel and Fischer, *Abstr.*, 1897, i, 611); it yields two *isooximes*: the  $\alpha$ -*isooxime* crystallises in prisms and melts at 111—112°; the more soluble  $\beta$ -*isooxime* melts at 82—84°.

In addition to the  $\alpha$ -*isooxime* melting at 115—116° (*Abstr.*, 1902, i, 805), a more soluble  $\beta$ -*isooxime*, melting at 106—108°, has been obtained from the oxime of 2:4:4-trimethyl*cyclohexanone*.

[With KARL HÜTTNER and JOHANNES ATTENBURG.]—The base boiling at 273°, obtained by treating 1:3-methyl*cyclohexanone* with ammonium formate (this vol., i, 160; see also *Abstr.*, 1898, i, 485; Tutin and Kipping, *Trans.*, 1904, 85, 65), consists of two stereoisomeric bases, which are separated by fractional precipitation from the ethereal solution by means of formic acid, the formate of  $\alpha$ -dimethyl*cyclohexylamine* being thrown down before that of the  $\beta$ -stereoisomeride.

$\alpha$ -Dimethyl*cyclohexylamine* is obtained as an oil, which boils at 273° and forms with water a solid *hydrate*; this melts at 46—48° and liquefies, losing water over sulphuric acid in a desiccator. The *hydrochloride* melts at 285°. The *benzoyl* derivative,  $N(C_7H_{13})_2Bz$ , crystallises from alcohol in plates, melts at 141°, and has  $[\alpha]_D - 34.646^\circ$ ; the *nitroso*-derivative,  $C_{14}H_{26}ON_2$ , crystallises from methyl alcohol, melts

at 83—84°, and has  $[\alpha]_D - 34^\circ$ ; the *phenylcarbamyl* derivative,  $N(C_7H_{13})_2 \cdot CO \cdot NHPH$ , melts at 174—176°.

$\beta$ -Dimethylcyclohexylamine is obtained as an oil which boils at 273° and does not form a hydrate; the *hydrochloride* melts at 211°; the *nitrate* and the *nitrite* are sparingly soluble. The *benzoyl* derivative melts at 151° and has  $[\alpha]_D - 11.877^\circ$ ; the *nitroso*-derivative, melting at 62—70°, and the *phenylcarbamyl* derivative, melting at 137—138°, have smaller molecular rotations than the corresponding  $\alpha$ -derivatives.

G. Y.

**Action of *o*-Nitrobenzaldehyde on Phenols in Presence of Hydrogen Chloride.** THEODOR ZINCKE and K. SIEBERT (*Ber.*, 1906, 39, 1930—1938. Compare Zincke and Preuntzell, this vol., i, 110; Schillinger and Wleügel, *Abstr.*, 1884, 60).—4-Chloro-2-*p*-hydroxy-phenylanthroxan,  $C_6H_3Cl \left\langle \underset{N}{\overset{C(C_6H_4 \cdot OH)}{\mid}} \right\rangle O$ , is prepared by satu-

rating a solution of *o*-nitrobenzaldehyde and phenol in glacial acetic acid or methyl or ethyl alcohol, cooled by ice, with hydrogen chloride, or by the action of phosphorus oxychloride on the glacial acetic acid solution; it crystallises in yellow needles, melts at 241°, sublimates without decomposition when heated carefully, is readily soluble in alcohol or acetic acid, but is only sparingly so in ether or benzene, and dissolves in aqueous sodium hydroxide, forming an orange-yellow solution. The dilute alcoholic solution becomes strongly fluorescent on addition of ammonia or an alkali hydroxide. The *acetyl* derivative,  $C_{13}H_7O_2ClNaAc$ , crystallises in broad, colourless needles and melts at 171°.

Reduction of the anthroxan by hydriodic acid and phosphorus leads to the formation of 5-chloro-2-amino-4'-hydroxybenzhydrol, or by tin and hydrochloric acid in alcoholic or glacial acetic acid solution to the formation of [5-chloro-2-amino-4'-hydroxybenzophenone],  $NH_2 \cdot C_6H_3Cl \cdot CO \cdot C_6H_4 \cdot OH$ . *see infra*

This crystallises in glistening, colourless needles, melts at 174°, and dissolves readily in alcohol, in glacial acetic acid forming a red, or in aqueous alkali hydroxides forming a yellow, solution. The *nitrate* and *sulphate* are readily soluble, but the *hydrochloride*, which crystallises in yellow needles, is insoluble in dilute acids. The *diacetyl* derivative,  $C_{17}H_{14}O_4NCl$ , crystallises in stout, white needles or leaflets and melts at 140°. The action of nitric acid of sp. gr. 1.5 on the amine leads to the formation of an unstable *product*, which is probably a mixture of two nitro-derivatives. When diazotised and coupled with  $\beta$ -naphthol, the amine yields a red *dye*; when boiled, the diazonium sulphate solution evolves nitrogen and yields a *product* which is soluble in aqueous alkali hydroxides; the diazonium chloride is reduced by stannous chloride, forming a yellow precipitate which resinifies when filtered. The *perbromide*,  $C_{13}H_6OClBr_3$ , prepared from the diazonium chloride, crystallises in red needles and melts at 198°.

5-Chloro-4'-hydroxybenzophenone,  $C_6H_4Cl \cdot CO \cdot C_6H_4 \cdot OH$ , formed by the action of amyl nitrite on the amine, crystallises in white needles, melts at 161°, and dissolves readily in alcohol, glacial acetic acid, or



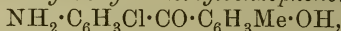
aqueous alkali hydroxides. The *acetyl* derivative,  $C_{15}H_{11}O_3Cl$ , crystallises in white needles and melts at  $108^\circ$ .

5-*Chloro-4'-hydroxybenzhydrol*,  $C_6H_4Cl \cdot CH(OH) \cdot C_6H_4 \cdot OH$ , is prepared by reduction of the ketone by means of sodium amalgam in dilute alkaline solution; it crystallises in white needles and melts at  $125^\circ$ .

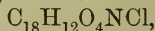
4-*Chloro-2-p-hydroxy-m-tolylanthroxan*,  $C_6H_3Cl \left\langle \begin{array}{c} C(C_7H_6 \cdot OH) \\ N \end{array} \right\rangle O$ ,

formed from *o*-nitrobenzaldehyde and *p*-cresol, crystallises from alcohol in light yellow needles and melts at  $210^\circ$ ; the *alkali* salts crystallise in glistening, orange-yellow leaflets. The *acetyl* derivative,  $C_{16}H_{12}O_3NCl$ , crystallises in white, glistening leaflets and melts at  $135^\circ$ .

5-*Chloro-2-amino-2'-hydroxy-4'-methylbenzophenone*,



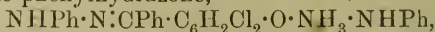
formed by reduction of the anthroxan by tin and hydrochloric acid, crystallises in yellow needles, melts at  $115^\circ$ , and dissolves in aqueous alkali hydroxides, forming yellow solutions; the *sodium* salt crystallises in glistening, golden leaflets. The *hydrochloride* forms colourless needles and is hydrolysed by water. The *diacetyl* derivative,



crystallises in yellow needles and melts at  $151^\circ$ . The action of ethyl nitrite on the amine leads to the formation of a *substance* which separates from alcohol in yellow crystals, and when heated with nitric acid of sp. gr. 1.4 yields 7-*chloro-1:9-dinitro-2-methylacridone*. This is formed also by treatment of the amino-compound with nitric acid of sp. gr. 1.4; it crystallises in glistening, yellow needles, melts at  $250^\circ$ , and is insoluble in aqueous, but dissolves in aqueous-alcoholic sodium hydroxide, forming a deep red solution, which deposits the *sodium* salt in violet needles, decomposed by water. G. Y.

**Action of Benzene and Aluminium Chloride on Free Phenol-carboxylic Chlorides.** RICHARD ANSCHÜTZ (*Annalen*, 1906, 346, 381—391).—[With JEFF H. SHORES.]—3:5-*Dichloro-2-hydroxybenzophenone*,  $OH \cdot C_6H_2Cl_2 \cdot CPh$ , is prepared by heating 3:5-dichlorosalicylic chloride with aluminium chloride and benzene in a reflux apparatus and treating the product with dilute hydrochloric acid; it crystallises from alcohol in yellow needles, melts at  $116^\circ$ , is readily soluble in cold benzene or hot alcohol, but dissolves to only a slight extent in water, forming a yellow solution, and with aqueous sodium hydroxide forms a reddish-yellow solution of the *sodium* derivative.

The action of phenylhydrazine on the ketone leads to the formation of (a) the *phenylhydrazone*,  $OH \cdot C_6H_2Cl_2 \cdot CPh : N \cdot NHPh$ , which crystallises from 96 per cent. alcohol in stellate aggregates of yellow needles, melts at  $186^\circ$ , and is insoluble in water, and (b) the *phenylhydrazonium* derivative of the phenylhydrazone,



which crystallises from benzene in long, white, woolly needles. The *oxime*,  $OH \cdot C_6H_2Cl_2 \cdot CPh : N \cdot OH$ , crystallises in light yellow, silvery needles and melts at  $196^\circ$ .

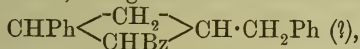
3:5-*Dichloro-2-hydroxybenzhydrol*,  $OH \cdot C_6H_2Cl_2 \cdot CHPh \cdot OH$ , prepared

by reduction of the ketone with 3 per cent. sodium amalgam in alcoholic solution, crystallises from light petroleum in thin, white needles and melts at  $94^{\circ}$ .

[With EMANUEL LÖWENBERG.]—3:5-Dibromo-2-hydroxybenzophenone,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{COPh}$ , formed by the action of aluminium chloride and benzene on 3:5-dibromosalicylic chloride, crystallises in long, yellow needles, melts at  $129\text{--}130^{\circ}$ , dissolves in aqueous sodium hydroxide forming a yellowish-green solution, and when treated with phenylhydrazine forms two phenylhydrazones. The stable *phenylhydrazone*,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{NHPh}$ , crystallises from dilute alcohol in yellow rhomboids and melts at  $176\text{--}177^{\circ}$ . The labile *modification*, which separates from the concentrated mother liquor from the stable form in white crystals, melts and resolidifies, changing into the stable modification at  $143^{\circ}$ . The labile *oxime*,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$ , formed by the action of hydroxylamine on the ketone in alcoholic solution, crystallises in white needles and melts and resolidifies at  $175^{\circ}$ , changing into the stable *oxime* which melts at  $199\text{--}201^{\circ}$ .

[With FRITZ SCHMITZ.]—3:5-Diiodobenzophenone,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{I}_2\cdot\text{COPh}$ , formed from 3:5-diiodosalicylic chloride, crystallises from alcohol in glistening, golden needles and melts at  $116^{\circ}$ . The *oxime*,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{I}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$ , *See errata* 1265  
crystallises in slightly yellow needles and melts at  $127^{\circ}$ . V. 90 G. Y.

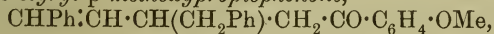
Action of a 50 per cent. Mixture of Glacial Acetic and Sulphuric Acids on  $\beta$ -Benzyl- $\beta$ -styrylpropiophenone and its Derivatives. HUGO BAUER and ERNST BREIT (*Ber.*, 1906, 39, 1916—1921. Compare Bauer, *Abstr.*, 1905, i, 278; Kohler, *ibid.*, 358).—When heated on the water-bath with a mixture of equal parts of glacial acetic and sulphuric acids,  $\beta$ -benzyl- $\beta$ -styrylpropiophenone undergoes isomerisation, being converted into a *substance*,



which crystallises from alcohol in colourless leaflets, melts at  $117^{\circ}$ , and remains unchanged when treated with potassium permanganate in acetone solution, but is oxidised slowly to carbon dioxide by aqueous permanganate at  $100^{\circ}$ . When heated with potassium hydroxide at  $300^{\circ}$ , it yields benzoic acid and an *acid*,  $\text{C}_{17}\text{H}_{18}\text{O}_2$ , which crystallises in slender, white needles, melts at  $169\cdot5\text{--}170^{\circ}$ , and is readily soluble in alcohol; the *barium* salt was analysed. The *oxime*,  $\text{C}_{24}\text{H}_{22}\cdot\text{N}\cdot\text{OH}$ , crystallises from alcohol and melts at  $166^{\circ}$ ; the *bromo*-derivative,  $\text{C}_{24}\text{H}_{21}\text{OBr}$ , crystallises in colourless needles and melts at  $161\cdot5^{\circ}$ .

*Cinnamylidene-p-methoxyacetophenone*,  $\text{C}_{18}\text{H}_{16}\text{O}_2$ , prepared by shaking *p*-methoxyacetophenone with cinnamaldehyde in aqueous sodium hydroxide solution, crystallises in light yellow needles, melts at  $95\cdot5\text{--}96\cdot5^{\circ}$ , is readily soluble in alcohol, ether, or acetone, and gives a cherry-red coloration with concentrated sulphuric acid. The *oxime*,  $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}$ , crystallises in colourless, glistening, silky leaflets, melts at  $131\cdot5^{\circ}$ , and is readily soluble in alcohol.

*$\beta$ -Benzyl- $\beta$ -styryl-p-methoxypropiophenone*,

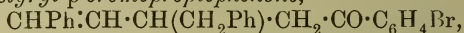


is prepared by adding ice-water to a mixture of the cinnamylidene-

compound and magnesium benzyl chloride in ethereal solution; it is obtained as a viscid oil, which solidifies under alcohol, forming white needles, melts at  $82.5^{\circ}$ , and gives a yellowish-green coloration with concentrated sulphuric acid. When heated with glacial acetic and sulphuric acids, it is converted into an *isomeride*,  $C_{25}H_{24}O_2$ , which forms glistening, white needles, melts at  $125^{\circ}$ , and is readily soluble in alcohol or acetone.

*Cinnamylidene-p-bromoacetophenone*,  $C_{17}H_{13}OBr$ , prepared from cinnamaldehyde and *p*-bromoacetophenone, crystallises from acetone in light yellow, matted needles and melts at  $149.5^{\circ}$ . The *oxime* forms colourless, silky leaflets and melts at  $184.5$ — $185.5^{\circ}$ .

*$\beta$ -Benzyl- $\beta$ -styryl-p-bromopropiophenone*,



separates from alcohol in white crystals, melts at  $114^{\circ}$ , and is readily soluble in alcohol or ether. The *isomeride*,  $C_{24}H_{21}OBr$ , crystallises in colourless leaflets and melts at  $112^{\circ}$ . G. Y.

**Constitution of  $\alpha$ - and  $\beta$ -Benzopinacolins.** MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1906, 62—70).—A critical *résumé* is given of the known facts regarding the chemistry of the two benzopinacolins (Abstr., 1891, 456; 1896, i, 662; Klinger and Lonnes, Abstr., 1896, i, 691; and Werner and Grob, Abstr., 1904, i, 864), and it is pointed out that the data at present available are insufficient to permit of a formula being definitely assigned to each of these two substances. The author is of opinion that only one benzopinacolin exists and that the variations in structure are not due, as he and others have supposed, to isomerisation induced by the action of reagents, but to an equilibrium phenomenon. T. A. H.

**Constitution of Tribenzoylenebenzene.** ARTHUR MICHAEL (*Ber.*, 1906, 39, 1908—1915).—The constitution originally assigned to tribenzoylenebenzene is the correct one; truxene (tribenzylenebenzene) and allied compounds are derivatives of benzene and not of tetrane.

The preparation of tribenzoylenebenzene from the sodium derivative of ethyl 1:3-diketohydrindenecarboxylate is described.

The identity of tribenzoylenebenzene prepared from 1:3-diketohydrindene with that prepared from phthalylacetic acid is based essentially on the similarity in physical properties.

The anhydride,  $C_{18}H_{10}O_3$ , prepared by the action of phosphorus oxychloride on phenylpropionic acid according to Lanser, is identical with the product which Michael and Bucher obtained by the action of acetic anhydride on phenylpropionic acid. When this anhydride is dissolved in alkali, it readily forms salts of the dibasic acid,  $C_{18}H_{12}O_4$ , and when the alkaline solution is acidified, the acid separates and not the anhydride, as Michael and Bucher originally supposed. The acid,  $C_{18}H_{12}O_4$ , is moderately stable and does not form an appreciable amount of anhydride when heated at  $100^{\circ}$ ; anhydride formation takes place rapidly at  $155$ — $165^{\circ}$ .

Phenylnaphthalenedicarboxylic acid (Lanser's "diphenyltetrenedicarboxylic acid") is shown to be quite distinct from phenenyltribenzoic acid.



The solubility of the acids in alcohol, glacial acetic acid, and ether respectively is different; the difference between the acids is also indicated by the comparison of their salts quoted. Further, a fluorescein is formed when phenylnaphthalenedicarboxylic acid is fused with resorcinol; phenenyltribenzoic acid does not form a fluorescein.  $\alpha$ -Phenylnaphthalene may be isolated from phenylnaphthalenedicarboxylic acid by heating a mixture of the barium salt with barium hydroxide, whilst the hydrocarbon resulting from phenenyltribenzoic acid is triphenylbenzene.

A. McK.

**Preparation of Amino-, Alkylamino-, and Arylamino-anthraquinones and their Derivatives.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 165728).—1-Dimethylamino-5-phenoxyanthraquinone,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_5$ , prepared by heating the diphenyl ether of anthrarufin with a 10 per cent. solution of dimethylamine in pyridine at 110—115°, separates from alcohol in red crystals and melts at 147—149°.

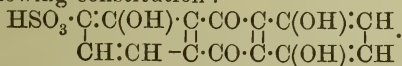
1-Dimethylamino-8-phenoxyanthraquinone, which separates from alcohol in thick crystals melting at 127—128°, is obtained similarly from the diphenyl ether of chrysazin. This ether also gives rise to 1-phenylamino-8-phenoxyanthraquinone, which crystallises from pyridine in long, lustrous needles and melts at 173—174°.

This patent contains several other examples of the substitution of a phenoxy-group by a substituted amino-radicle. In two instances, two amino-groups were introduced into the aromatic nucleus. Thus, 1-phenoxyanthraquinone-5-sulphonic acid when heated with solutions of methylamine and ammonia gave rise to 1:5-dimethyldiaminoanthraquinone and 1:5-diaminoanthraquinone respectively.

G. T. M.

**Preparation of Polyhydroxyanthraquinonesulphonic Acids.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 165860).—When the polyhydroxyanthraquinones are sulphonated according to the usual processes, mixtures of sulphonic acids are produced which are difficult to separate, and, moreover, oxidation readily occurs with the introduction of more hydroxyl groups (compare this vol., i, 294). The result is quite different in the presence of boric acid. In this case, homogeneous products are obtained without oxidation.

1:4:5-Trihydroxyanthraquinone, mixed with an equal weight of boric acid, is treated with twenty parts of fuming 30 per cent. sulphuric acid, at 130°; the product when poured into water gives the free sulphonic acid which is transformed into its acid sodium salt, which separates in orange-red crystals. The new sulphonic acid has probably the following constitution:



Alizarin-bordeaux when sulphonated in this way also gives rise to a monosulphonic acid.

G. T. M.



Presence of *l*-Borneol in the Ethereal Oil from the Buds of *Pinus maritima*. E. BELLONI (*Chem. Centr.*, 1906, i, 1552; from *Boll. Chim. Farm.*, 45, 185—187).—The presence of *l*-borneol in the oil from *Pinus maritima* has been detected by the method X of Tiemann and Krüger (*Abstr.*, 1896, i, 382). In the following table, the physical constants and composition of four samples of oil are given: I and II were prepared from fresh buds, and III and IV partly from dried buds.

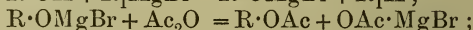
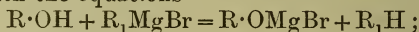
	I.	II.	III.	IV.
Yield from buds .....	0·856	0·867	0·841	0·892
Sp. gr. at 15° .....	0·8797	0·8805	0·889	0·8848
[ $\alpha$ ] <sub>D</sub> at 15° .....	-29·4°	-30·48°	-24·45°	-26·17°
<i>n</i> <sub>D</sub> at 20° .....	1·4795	1·4812	1·482	1·478
Free acid calculated as octoic acid...	0·30 %	0·28 %	0·97 %	0·59 %
Esters as bornyl acetate .....	1·58	1·12	1·67	1·37
Free alcohol ( <i>l</i> -borneol) .....	5·08	6·78	5·19	7·83
Combined alcohol .....	1·25	0·89	1·31	1·07
Total alcohol .....	6·33	7·67	6·50	8·90

E. W. W.

Chemistry of Bornyl- and Fenchyl-alcohols. IWAN L. KONDAKOFF (*Chem. Zeit.*, 1906, 30, 497—499). Compare *Abstr.*, 1904, i, 755).—A critical discussion regarding the probable constitution of these substances.

P. H.

Esterification of Alcohols and Phenols. JOSEF HOUBEN (*Ber.*, 1906, 39, 1736—1753).—The Grignard reagents are employed, in accordance with the equations



Magnesium alkyl bromides give satisfactory results in the case of saturated primary aliphatic alcohols or phenols, but the unsaturated alcohols, geraniol, linalool, and terpineol, in these circumstances, yield esters which are coloured, contain halogen, and quickly resinify. With such alcohols better results are obtained with magnesium benzyl chloride, but best of all with magnesium alkyl chlorides, when the reaction proceeds almost quantitatively and the ester obtained after fractionation is colourless, free from halogen, and does not exhibit any tendency to become resinous. The operation is performed as follows: the alcohol is slowly added to the cold ethereal solution containing magnesium ethyl or methyl chloride in excess of the theoretical quantity; after keeping at the ordinary temperature for twelve to twenty-four hours, the mixture is well cooled and an excess of acetic anhydride added drop by drop. After one hour, the mixture is decomposed by ice and acetic acid, the ethereal layer removed, dried over potassium carbonate, and the ester fractionated under reduced pressure after evaporation of the ether.

*Linalyl propionate* is a colourless liquid with an odour of lilies of the valley, and boils at 108—111° under 12 mm. or at 115—119° under 16 mm. pressure.

*Terpinyl propionate* is a pleasant-smelling liquid which boils at 119—121° under 11·5 mm. pressure. *Cis*-terpin yields a *diacetate*,

which boils at 140—141° under 10 mm. pressure and has only a faint odour, differing in these respects from Oppenheim's terpin diacetate (*Annalen*, 1864, 129, 157), which is probably a mixture of terpinyl acetate, acetic acid, and dipentene, into which the diacetate decomposes when distilled under the ordinary pressure. The terpinyl acetate obtained from this mixture is a different substance from that obtained directly from terpineol.

C. S.

**Preparation of the Terpinoid Alcohol, Nerol.** HEINE & Co. (D.R.-P. 165894, 165895, 165896. Compare this vol., i, 295).—Nerol is prepared from linalool by the following series of operations: the latter oil was dissolved in glacial acid, treated in the cold with concentrated sulphuric acid dissolved in the same solvent, the oily product washed with water and hydrolysed with alcoholic potash on the water-bath. The hydrolysed oil was distilled in steam and then fractionated under reduced pressure; the less volatile products, consisting of terpineol, geraniol, and nerol, were boiled with phthalic anhydride and benzene, whereby the primary alcohols only were converted into the corresponding acid phthalates. After removing the excess of unchanged anhydride by cooling and adding light petroleum, the solution was distilled and the residual acid phthalates dissolved in dilute aqueous sodium carbonate. The alkaline solution was washed with ether, acidified with dilute sulphuric acid, and the acid phthalates extracted with ether and hydrolysed with alcoholic potash at the ordinary temperature or on the water-bath. The resulting alcohols, geraniol and nerol, were distilled in steam or under diminished pressure and finally separated by means of dry calcium chloride, which yields with geraniol a compound insoluble in light petroleum. The yield of rectified nerol was about 5—10 per cent.

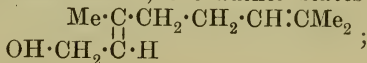
The initial esterification can be accomplished likewise with acetic anhydride, the yield by this method being 15—20 per cent. Other acetylating agents may be employed, such as acetic acid with sodium acetate, ferric chloride, or phosphoric acid. Linalyl acetate and the ethereal oils containing this ester are also amenable to this process of separation.

G. T. M.

**Nerol and its Preparation from Linalool.** OTTO ZEITSCHEL (*Ber.*, 1906, 39, 1780—1792).—When *l*-linalool (Barbier's licarhodol, *Abstr.*, 1893, i, 544) is treated with acetic anhydride, formic acid, or sulphuric and acetic acids (Stephen, *Abstr.*, 1899, i, 68), nerol can be isolated in quantities varying from 3 to 10 per cent.; dilute mineral acids act on linalyl acetate to give a similar poor yield of nerol.

When an alcoholic solution of citral is reduced with sodium amalgam, the resinifying action of the alkali being prevented by the addition of acetic acid drop by drop, geraniol and nerol are produced to the extent of 12 and 7 per cent. respectively. The oxidation of nerol or geraniol by chromic and sulphuric acids yields citral and a substance with the odour of methylheptenone.

Basing his conclusions mainly on these results, the author states that geraniol has the constitution



nerol,  $\text{Me} \cdot \overset{\text{H}}{\underset{\text{H}}{\text{C}}} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{CMe}_2$ ; and that citral *a* is identical with geranial and citral *b* with neral.

Terpin hydrate was isolated from the products of the reaction between nerol or geraniol and 5 per cent. sulphuric acid after two hundred hours' shaking (Tiemann, Abstr., 1895, i, 639). The acetates are practically unchanged by this treatment, whilst the linalyl ester is converted more slowly into terpineol and terpin hydrate.] C. S.

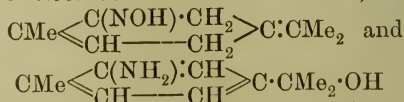
**Identity of Natural and Artificial Nerols.** HUGO VON SODEN and WALTER TREFF (*Ber.*, 1906, 39, 1792—1793. Compare preceding abstract).—Nerol, obtained from linalool and freed as much as possible from geraniol by calcium chloride, is converted into the diphenylurethane, which is crystallised from light petroleum (Abstr., this vol., i, 295). The recovered nerol agrees in all its properties and in the characteristics of its compounds with the alcohol obtained from natural sources. C. S.

**Preparation of the Hydrates of Unsaturated Organic Compounds.** KNOLL & Co. (D.R.-P. 165726).—*Citronellidineacetone hydrate* was obtained by boiling together citronellidineacetone and sodium hydrogen sulphite in aqueous solution, then adding dilute acid, and leaving the mixture for several days, after which the intermediate bisulphite compound was decomposed by sodium hydroxide. The hydrate thus liberated when fractionated under reduced pressure boiled at 175° under 12 mm. pressure.

*Carvone hydrate* was similarly produced by the successive action of sodium hydrogen sulphite, dilute sulphuric acid, and sodium hydroxide; it boils at 153—154° under 12 mm. pressure and melts at 43°. Its semicarbazone melts at 177° and its oxime at 113°.

*Ethyl citrylidenemalonate hydrate*, obtained in a similar manner from ethyl citrylidenemalonate, boils at 215—225° under 12 mm. pressure and has a sp. gr. 1.022 at 20°. G. T. M.

**Terpenes and Ethereal Oils.** LXXX. *iso*Carvoxime and the Constitution of Carvoline. Remarks on the Mechanism of the Isomerisation of Oximes. OTTO WALLACH (*Annalen*, 1906, 346, 266—285. Compare Goldschmidt and Kisser, Abstr., 1887, 475, 923; Goldschmidt, Abstr., 1893, i, 723).—The author discusses the constitution of *isocarvoxime* and of carvoline, and ascribes to these the formulæ



respectively; the formation of the latter from the former is compared with that of aminothymol from carvoxime. These changes, which resemble that of phenylhydroxylamine into aminophenol, may be explained by the Beckmann reaction, if this is considered to take place through the intermediate formation of a nitrogen heterocyclic group.



[With HERMANN LAUTSCH.]—*iso*Carvoxime was prepared by shaking carvoxime with hydrogen bromide in glacial acetic acid solution and heating the product with sodium methoxide in methyl-alcoholic solution. With bromine it forms a *dibromide*,  $C_{10}H_{15}ONBr_2$ , melting and decomposing at 126—127°, and a *tetrabromide*,  $C_{10}H_{15}ONBr_4$ , melting at 134—135°.

Carvoline (Goldschmidt, *loc. cit.*) is formed together with carvacrol when *isocarvoxime* is boiled with dilute sulphuric, acetic, or oxalic acid; it crystallises in colourless needles or prisms, boils at 158—163° under 12 mm. or at 289—290° under the ordinary pressure, and is not volatile in a current of steam; the *hydrochloride* melts at 189—190°. When boiled with fuming hydriodic acid in a reflux apparatus, the base yields carvacrylamine. Carvoline forms dyes when diazotised and coupled with phenols: the *product* with  $\beta$ -naphthol,  $OH \cdot C_{10}H_{12}N_2 \cdot C_{10}H_7O$ , crystallises in deep red needles, melts at 171°, and is insoluble in aqueous alkali hydroxides. The *diazonium sulphate* obtained from carvoline is decomposed by boiling water, forming a *phenol* which yields a deep yellowish-brown dye when coupled with diazotised sulphanilic acid in alkaline solution. The *chloro-derivative*,  $CMe \begin{smallmatrix} \text{<CCl:CH>} \\ \text{CH:CH} \end{smallmatrix} C \cdot CMe_2 \cdot OH$ , formed from carvoline by Sandmeyer's reaction, melts at 50—51°, boils at 245—249°, when treated with phosphorus pentachloride yields an oily *dichloride*, boiling at 230—234°, and is oxidised by chromic acid to *o-chloro-p-acetyltoluene*,  $C_6H_3MeCl \cdot COMe$ . This has an odour of acetophenone, melts at 45—46°, boils at 250—254°, and is volatile in a current of steam. The crystalline *semicarbazone* melts at 237—238°; the *oxime*,  $C_6H_3Cl \cdot CMe \cdot N \cdot OH$ , forms white leaflets and melts at 96—97°. When treated with a hypobromite solution, the ketone is oxidised to *o-chloro-p-toluic acid*. G. Y.

**Synthesis of Camphor Derivatives.** *iso*Laurelone and *iso*-Lauronolic Acid ( $\beta$ -Campholytic Acid). GUSTAVE BLANC (*Compt. rend.*, 1906, 142, 1084—1086).—*aa*-Dimethyladipic acid was prepared as already described (Abstr., 1905, i, 680), except that ethyl  $\gamma$ -bromo-*aa*-dimethylbutyrate,  $CH_2Br \cdot CH_2 \cdot CMe_2 \cdot CO_2Et$ , was condensed with ethyl malonate in place of ethyl sodiocyanoacetate. The acid was warmed with acetic anhydride and the resulting anhydride converted by distillation into *dimethylcyclopentanone*,  $\begin{smallmatrix} CH_2 \cdot CH_2 \\ | \quad \quad | \\ CH_2 - CO \end{smallmatrix} > CMe_2$ . This is a mobile liquid, has a camphoraceous odour, and melts at 143°; its *semicarbazone* melts at 190°. The ketone on treatment with magnesium methyl iodide yields the *tertiary alcohol*,  $\begin{smallmatrix} CH_2 \cdot CMe_2 \\ | \quad \quad | \\ CH_2 - CH_2 \end{smallmatrix} > CMe \cdot OH$ , which crystallises in long needles, melts at 37°, boils at 60° under 15 mm. pressure, and possesses a musty, camphoraceous odour. When distilled under atmospheric pressure, it decomposes into water and *iso*-laurelone,  $\begin{smallmatrix} CH_2 \cdot CH_2 \\ | \quad \quad | \\ CH = CMe \end{smallmatrix} > CMe_2$ . The hydrocarbon is transformed by condensation with acetyl chloride in presence of aluminium chloride



into a *ketone*, which is reduced by sodium to the secondary *alcohol*,  $\text{CMe}_2 \cdot \text{CHMe} \cdot \text{CH}_2 - \text{CH}_2 > \text{CH} \cdot \text{CHMe} \cdot \text{OH}$ , which boils at 90—95° under 10 mm. pressure, and this on oxidation by nitric acid gives dihydro*isolauro*nolic acid, which on bromination in the  $\alpha$ -position and subsequent elimination of hydrogen bromide gives *isolauro*nolic acid.

T. A. H.

**Ethereal Oils.** HEINRICH HAENSEL (*Chem. Centr.*, 1906, i, 1497; from *Geschäftsber.*, March, 1906. Compare Abstr., 1903, i, 187).—Silver fir oil from Lower Austria has almost the same sp. gr. as the Tyrolese oil, but it has a less rotatory power and contains a smaller quantity of esters; it has sp. gr. 0.8761—0.8776 at 15°,  $[\alpha]_D - 35.99^\circ$  to  $-37.14^\circ$  at 15°, and contains 4.46—5.22 per cent. of esters calculated as bornyl acetate. The fruit from which the seeds have been removed yields 0.038 per cent. of an orange-coloured oil which has a strong odour of the fruit and an acid reaction: it has a sp. gr. 0.90735 at 20°,  $[\alpha]_D + 0.40^\circ$  at 19° (10 per cent. benzene solution), and acid number 22.1. The oil contains aldehydes, and a stearoptene is precipitated on the addition of absolute alcohol.

Dried garden rue yields 0.135 per cent. of a dark brown, ethereal oil which has a very strongly acid reaction and on rectification forms a pale greenish-yellow oil, which has a sp. gr. 0.8487 at 20°,  $[\alpha]_D + 0.64^\circ$  at 20°, and ester number 119; the acetyl derivative has ester number 157. When shaken with a solution of sodium hydrogen sulphite, the oil does not yield an additive compound.

E. W. W.

**Ethereal Oils.** SCHIMMEL & Co. (*Chem. Centr.*, 1906, i, 1497—1498; from *Geschäftsber.*, April, 1906. Compare Abstr., 1905, i, 536).—Lemon-yellow cedar oil from Haiti has an odour similar to that of ordinary cedar oil, sp. gr. 0.9612 at 15°,  $[\alpha]_D - 14.58'$ , acid number 2.7, and ester number 5.0; the acetyl derivative has ester number 64. Fennel oil contains camphene and phellandrene, but not cymene (compare Tardy, Abstr., 1897, i, 578). Templin oil prepared from Styrian material has a sp. gr. 0.8685 at 15°,  $[\alpha]_D - 11.3'$ , acid number 1.4, and ester number 16.8 (= 5.9 per cent. bornyl acetate); 67 per cent. of the oil distils at 170—203°. Styrian silver fir oil has sp. gr. 0.8852 at 15°,  $[\alpha]_D - 34.55'$ , and ester number 17.5 (= 6.1 per cent. bornyl acetate); 55 per cent. of the oil distils at 162—185°. Two black pine oils prepared from needles of *Pinus Laricio* have sp. gr. 0.8646 and 0.8701 at 15°,  $[\alpha]_D + 8.17'$  and  $+3.29'$ , and ester numbers 2.9 and 9.8 respectively. Bay-leaf oil contains linalool and the methyl ether of eugenol. Bright yellow sassafras oil prepared from the roots of *Sassafras officinalis* dissolves in 1—2 volumes of 90 per cent. alcohol, and has a sp. gr. 1.075 at 15°,  $[\alpha]_D + 2.14'$ , and ester number 1.9. Solidago oil, or oil of Golden Rod, is pale yellow, and has a pleasant, refreshing odour; it has a sp. gr. 0.8904 at 15°,  $[\alpha]_D + 15.34'$ , and ester number 34.2 (acetyl derivative 59.9). The esters probably consist mainly of bornyl acetate. The bright olive-green oil from *Solidago nemoralis* has a peculiar odour, resembling that of

cypress oil; it has a sp. gr. 0.8799 at 15°,  $[\alpha]_D - 23^\circ 10'$ , and ester number 14.4 (acetyl derivative 38.2). Indian turpentine oil from the resinous balsam of *Pinus longifolia* is soluble in 7.5 volumes of 90 per cent. alcohol, and has a sp. gr. 0.8734 at 15°,  $[\alpha]_D + 3^\circ 13'$ , acid number 1.9, and ester number 1.3.

An ethereal oil which contains free fatty acids and constituents which cannot be saponified is obtained by extracting musk with ether and distilling in steam. The odour of musk is caused by the presence of a ketone, *muskone*,  $C_{15}H_{28}O$  or  $C_{16}H_{30}O$ , which boils at 327—330° and at 142—143° under 752 and 2 mm. pressure respectively; it has sp. gr. 0.9268 at 15°,  $[\alpha]_D - 10^\circ 6'$ , and  $n_D 1.47900$  at 25°. The *semicarbazone* melts at 133—134°. E. W. W.

**Ethereal Oil of the Buds of *Pinus maritima*.** E. BELLONI (*Chem. Centr.*, 1906, i, 360—361; from *Ann. Soc. Chim. Milano*, ii).—The fresh buds of *Pinus maritima* collected in S. France yield on distillation 0.517 per cent. of a bright green ethereal oil, which has a fresh, aromatic taste and the characteristic odour of pine needles; the dry buds yield 0.681 per cent. of a similar oil. The following data refer respectively to the oil from the fresh buds and to that from the dry buds. Sp. gr. at 15°, 0.8810 and 0.8963;  $[\alpha]_D$  at 15°,  $-26.518^\circ$  and  $-22.355^\circ$ ; acid numbers, 0 and 5.43; ester numbers, 7.90 and 8.27; saponification numbers, 7.90 and 13.70; esters, 2.77 and 2.92 per cent.; combined alcohols, 2.13 and 2.28 per cent. The oil from the dried buds also contained 11.90 of uncombined alcohols and a total of 14.18 per cent. of alcohols. The oil is miscible with 95—100 per cent. alcohol, is soluble in 10 parts of 90 per cent. alcohol, but insoluble in 80 per cent. alcohol, and does not contain aldehydes. The free acids consist mainly of hexoic acid, of which the oil contains 1.396 per cent., and the esters appear to be acetates, propionates, hexoates, and laurates. *l*-Pinene is the chief constituent of the oil. When the alcoholic solution of *l*-pinene nitrosochloride is heated with piperidine for a long time on the water-bath, needle-shaped crystals of nitrosopinene separate from the product after some days. Neither phellandrene nor silvestrene could be detected in the fraction of the oil boiling at 170—190°, but limonene appeared to be present either in the form of one of the two active modifications or in the inactive form as dipentene. Although the odour of the oil indicates the presence of ethers of borneol, attempts to isolate these compounds from the fractions boiling at 190—260° failed. E. W. W.

**The Constituents of the Gutta-percha from *Palaequium treubi*.** ÉMILE JUNGFLEISCH and HENRI LEROUX (*Compt. rend.*, 1906, 142, 1218—1221).—The crude gutta of the leaves of *Palaequium treubi* contains a crystalline principle, *paltreubin*,  $C_{30}H_{50}O$ , which remains dissolved when the hot toluene extract of the leaves is treated with alcohol in order to precipitate the hydrocarbon of the gutta, and is separated by evaporating the mother liquor to dryness, extracting the wax from the residue by means of hot alcohol, and finally recrystallising from benzene. *Paltreubin* forms colourless, silky needles belonging to the monoclinic system (Wyrouboff), it melts at 260°, and

sublimes at  $230^{\circ}$ , forming characteristic elongated prisms; it is almost insoluble in all the ordinary organic solvents except toluene or benzene, and its solutions are optically inactive. Paltreubin is completely esterified when heated with excess of acetic anhydride in sealed tubes at  $175^{\circ}$ ; the product consists of two isomeric acetates from which two alcohols, each isomeric with the original, are obtained by saponification.

*$\alpha$ -Paltreubyl acetate*,  $C_{30}H_{49} \cdot OAc$ , melts at  $235^{\circ}$ , is soluble in ether, and can be recrystallised from benzene in the form of voluminous crystals or monoclinic prisms (Wyrouboff); its solutions are optically inactive, and it yields  *$\alpha$ -paltreubyl alcohol*,  $C_{30}H_{49} \cdot OH$ , on saponification with alcoholic potassium hydroxide, which crystallises from benzene in needles melting at  $190^{\circ}$ .  *$\beta$ -Paltreubyl acetate*,  $C_{30}H_{49} \cdot OAc$ , melts at  $290^{\circ}$ , is sparingly soluble in ether, crystallises from benzene in well-developed, colourless prisms belonging to the monoclinic system, but different from those of the  $\alpha$ -isomeride (Wyrouboff);  *$\beta$ -paltreubyl alcohol*,  $C_{30}H_{49} \cdot OH$ , obtained from the preceding compound by saponification with alcoholic potassium hydroxide, crystallises from benzene in long, thin needles, melts at  $295^{\circ}$ , and sublimes at  $270$ – $275^{\circ}$ , forming thin, prismatic needles, and is identical with an alcohol which the authors have extracted from the leaves of *P. gutta* or *P. borneese*, or from a residue obtained in the commercial preparation of gutta from leaves.

Paltreubin and  $\alpha$ - and  $\beta$ -paltreubyl alcohol are isomeric with  $\alpha$ - and  $\beta$ -amyrin (Vesterberg, Abstr., 1887, 733; 1891, 165). M. A. W.

**Sapotoxin and Sapogenin from *Agrostemma githago*.** JOSEF BRANDL [with E. MAYR and A. VIERLING] (*Chem. Centr.*, 1906, i, 1350–1353; from *Arch. exp. Path. Pharm.*, 54, 245–284).—The seeds of *Agrostemma githago* contain 6.44 per cent. of fat and yield 4.9–6.1 of crude sapotoxin. 18.1 per cent. of pure sapotoxin is obtained from the crude product by extraction with absolute alcohol, the insoluble residue consisting of a higher sapotoxin. The pure sapotoxin is dull brownish-yellow and contains C 54.23 per cent., H 7.23, and O 38.54; it forms a bright yellow solution in water, and the rotatory power of a 2 per cent. solution in a 20 cm. tube is  $+0.22^{\circ}$ . A determination of the molecular weight by Raoult's method gave 1810. Sapogenin, prepared by digesting sapotoxin with dilute sulphuric acid, contains 66.28 per cent. of carbon, 8.62 of hydrogen, and 25.10 of oxygen, crystallises from absolute alcohol in very small, slender needles, becomes yellow at  $190^{\circ}$ , sinters at  $210^{\circ}$ , and decomposes at  $220^{\circ}$ ; it is a saturated acid and liberates carbon dioxide from carbonates. The rotatory power of a 2 per cent. solution in sodium carbonate solution in a 20 cm. tube is  $+1.6^{\circ}$ . Molecular weight determinations by Raoult's method gave 605 and 648, and by the boiling point method 643 and 662. 51.92 per cent. of a sugar (calculated as dextrose) is also formed by the hydrolysis of sapotoxin; it is inactive, is scarcely attacked by yeast in twenty-four hours, and forms three osazones melting respectively at  $180^{\circ}$ ,  $203^{\circ}$ , and  $205^{\circ}$ . By the action of acetic anhydride on sapogenin, an acetyl derivative which crystallises from methyl alcohol is formed, together with a by-product which is soluble in water, gives a precipitate with lead acetate,



but has no hæmolytic action. The potassium and sodium salts of sapogenin crystallise in slender needles, and the potassium salt of methylsapogenin in very slender rods.

Sapogenin,  $C_{33}H_{52}O_{10}$ , prepared by the action of dilute sulphuric acid on quillajic acid or on quillajasapotoxin, crystallises from absolute alcohol in slender, white needles; a determination of the molecular weight by the boiling-point method gave 561.

The physiological action of *Agrostemma* sapotoxin and sapogenin is also described in some detail in the abstract.  
E. W. W.

**Products extracted from *Solanum sodomaeum*. II.** GIUSEPPE ODDO and AMEDEO COLOMBANO (*Gazzetta*, 1906, 36, i, 310—313. Compare Abstr., 1905, i, 455).—The authors describe a method for extracting solanine from *Solanum sodomaeum* more simply and in better yield than by the process formerly described (*loc. cit.*). The berries are well pounded in a marble mortar and are then macerated for twenty-four hours with sufficient 2·5 per cent. sulphuric acid solution to cover them completely. The solution is then filtered through flannel, the filtrate rendered alkaline with sodium or potassium hydroxide solution and the precipitated solanin filtered through flannel, washed well with water, dried, and treated with alcohol as previously described.

The neutralised acid extract is found to contain also a compound which crystallises from water in aggregates of small, reddish-yellow prisms, beginning to melt at 195° and completely melting and decomposing at 215°. Its aqueous solution is coloured green by ferric chloride solution and an intense blood-red by alkali. Alkali carbonate solutions dissolve it, giving brownish-yellow liquids.  
T. H. P.

**Solanine and other Constituents of the Berries of *Solanum sodomaeum* from Sicily.** ARTURO SOLDAINI (*Chem. Centr.*, 1906, i, 563; from *Boll. Chim. Farm.*, 1905, 44, 769—773, 808—810, and 843—885).—The author concludes that neither he nor Oddo and Colombano (Abstr., 1905, i, 455) have yet been dealing with the pure alkaloid (glucoside), and therefore many of his previously published results require modification.  
P. H.

**Aloxanthin.** OTTO A. OESTERLE (*Chem. Centr.*, 1906, i, 367—368; from *Schweiz. Woch. Pharm.*, 43, 682—684. Compare Abstr., 1899, i, 538).—Alochrysin is not a homogeneous compound, since the acetyl derivative can be separated into two components, of which the one is insoluble in benzene and a derivative of rhein, whilst the other is a derivative of aloemodin. It is probable that emodin is first formed by the action of potassium dichromate and sulphuric acid on aloin and is then oxidised to rhein. It should doubtless be possible to obtain emodin in this way.  
E. W. W.

**Condensation Products of Tannic Acid with Formaldehyde and Acid Amides.** ARNOLD VOSWINKEL (D.R.-P. 165980).—The condensation products of tannic acid with formaldehyde and acid amides have the general formula  $C_{14}H_9O_9 \cdot CH_2 \cdot NH \cdot COR$ .



The formamide derivative,  $C_{16}H_{13}O_{10}N$ , which was prepared by adding formaldehyde and formamide to a solution of tannic acid in dilute hydrochloric acid, forms a light brown powder insoluble in water or alcohol.

*Methylene-tannin-acetamide*,  $C_{17}H_{15}O_{10}N$ , was obtained similarly and resembles the preceding compound. The derivatives of amides sparingly soluble or insoluble in water were prepared in alcoholic solutions. These products are all soluble in aqueous solutions of sodium carbonate, borate, or acetate, and are regenerated on treatment with acids. The compounds have therapeutic properties similar to those of the carbamide derivatives.

G. T. M.

**Constitution of Methronic Acid.** HYPOLYT TREPHILIEFF (*Ber.*, 1906, 39, 1859—1862. Compare Fittig and Hantzsch, *Abstr.*, 1889, 126).—Ethyl methronate does not react with phenylhydrazine; the acid is oxidised by nitric acid to acetic and oxalic acids, combines with four atoms of bromine, and is hydrolysed to acetonylacetone. Under Fittig's conditions of preparation, 40 per cent. of the sodium succinate remains in the mother liquor without any ethyl acetoacetate, and the yield is only 30 per cent. of the theoretical; this is increased to 58 per cent. when 2 mols. each of ethyl acetoacetate and acetic anhydride are used for each mol. of sodium succinate. The by-products in the reaction are carbon dioxide, ethyl acetate, and acetone.

In accordance with these facts, methronic acid is regarded as having

the formula 
$$\begin{array}{c} C(CO_2H) \equiv CMe \\ CH:C(CH_2 \cdot CO_2H) > O. \end{array}$$

C. S.

**Synthesis of Simple Pyronones from Acid Haloids.** EDGAR WEDEKIND (*Chem. Centr.*, 1906, i, 369; from *Verh. Deut. Naturforsch. Aerzte*, 1904, ii, 81—83. Compare *Abstr.*, 1901, i, 639; 1902, i, 739).—When propionyl, phenylacetyl, or hydrocinnamoyl chloride acts on tertiary bases, the acid chloride residues unite to form trimeric condensation products. Hydrocinnamoyl chloride yields benzyldiphenyl pyronone, which reacts in accordance with the tautomeric formulæ

$$\begin{array}{ccc} CH_2Ph \cdot C : CPh \cdot CO & & CH_2Ph \cdot C : CPh \cdot C \cdot OH \\ | & \text{or} & | \\ O-CO-CHPh & & O-CO-CPh. \end{array}$$

The pyronone forms a sodium salt when treated with sodium hydroxide, and an oxime with hydroxylamine. By the action of acyl chlorides, acyl derivatives are obtained, and benzyldiphenyl dihydroxypyridine,

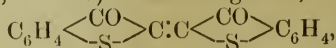
$$\begin{array}{c} CH_2Ph \cdot C - CPh - C \cdot OH \\ | \qquad \qquad | \\ N : C(OH) \cdot CPh \end{array}$$

is formed by the action of ammonia.

When isobutyl chloride acts on tertiary bases, a diketone of the tetramethylene series seems to be produced.

E. W. W.

**Thioindigo-red B.** R. WIRTHER (*Chem. Centr.*, 1906, i, 1353; from *Färberzeit.*, 17, 85—87).—Thioindigo-red,



manufactured by Kalle & Co., of Biebrich, resembles indigo in its method of application as a dye, its solubility in concentrated sulphuric

acid, and its slight solubility in organic solvents. It can be sublimed, and its solutions in chloroform, carbon disulphide, toluene, &c., have a yellowish-red fluorescence. Wool, silk, and cotton extract the colouring matter from the yellow solution formed by the action of reducing agents on the dye, and the red dye is regenerated when the fibres are exposed to air. Thioindigo-red may be used with a sodium sulphide bath, and may also be applied in cotton printing. E. W. W.

**Constitution of Adrenaline.** ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1906, 8, 95—120. Compare Abstr., 1904, i, 1069; also Takamine, Abstr., 1902, ii, 217; Aldrich, 1901, ii, 564; 1902, ii, 518; Abel, *ibid.*, 1903, i, 376; von Fürth, *ibid.*, 669; Pauly, 1904, i, 128, 540; Jowett, Trans., 1904, 85, 192; Bertrand, Stolz, 1905, i, 106).—A modified method for the preparation of von Fürth's adrenaline tribenzenesulphonate is described. In chloroform solution it has  $[\alpha]_D -15.12^\circ$ , but the rotation is somewhat less after it has been warmed with acetic acid. The presence of a free hydroxyl group has been shown by its conversion into the *m*-nitrobenzoate,  $C_{34}H_{28}O_{12}N_2S_3$ , which is doubly refracting. It begins to sinter at  $71^\circ$  and melts between  $80^\circ$  and  $86^\circ$ .

When adrenaline tribenzenesulphonate is oxidised with an acetic acid solution of chromic anhydride, it yields *adrenalone tribenzene-sulphonate*,  $(SO_2Ph \cdot O)_2C_6H_3 \cdot CO \cdot CH_2 \cdot NMe \cdot SO_2Ph$ , which may be purified by solution in acetic acid and precipitation with water. It dissolves sparingly in cold benzene or ethyl acetate and in hot alcohol, and is insoluble in ether, acids, or alkalis. It is optically inactive, and may be crystallised from acetic acid at  $0^\circ$ , and then separates from absolute alcohol in long, rhombic needles melting at  $106-107^\circ$ . Its *p*-nitrophenylhydrazone,  $C_{33}H_{28}O_{10}N_4S_3$ , melts at  $174-175^\circ$ .

The substance previously termed peradrenalone tribenzenesulphonate is shown to be a mixture of adrenalone and a more complex substance melting at  $196-197^\circ$ . It dissolves in ammonium hydroxide solution.

Adrenalone tribenzenesulphonate has been synthesised from methyl-aminoacetylcatechol. J. J. S.

**Quinine Tannate.** MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 1417; from *Collegium*, 1906, 108).—*Quinine tannate* forms a white, amorphous powder which melts at  $64^\circ$ ; it separates from a solution in alcohol to which 4—5 drops of acetic anhydride are added in crystals which melt at  $79-81^\circ$ . Since neither tannin nor gallic acid is formed when the tannate is hydrolysed, it cannot be a true salt, but is possibly a compound resembling a Schiff's base. E. W. W.

**Action of Gum Arabic on Morphine.** RICHARD FIRBAS (*Chem. Centr.*, 1906, i, 374; from *Pharm. Post.*, 38, 735—738. Compare Bourquelot, *J. Pharm. Chim.*, [vi], 19, 475).—An oxymorphine is formed by the action of a solution of gum arabic on morphine, although comparatively slowly, the action being dependent on the concentration of the solution and the time. If the quantity is not too small, the presence of oxymorphine may be detected by the precipitate which it gives with potassium chromate. The gum does

not appear, however, to have any action on opium powder or extract even when the substances are allowed to remain together in a moist condition for six weeks.

E. W. W.

**Morphine Alkylbromides.** J. D. RIEDEL (D.R.-P. 165898).—*Morphine methobromide*, prepared by shaking together for eight to twelve hours at 40–50° a mixture of finely-divided morphine, methyl bromide, and absolute alcohol, was recrystallised from water or dilute alcohol and separated in colourless needles, sintering at 260° and melting at 265–266°. It is only sparingly soluble in absolute alcohol or chloroform, and is insoluble in ether. The same salt was also obtained when finely-divided morphine was suspended in a mixture of chloroform and methyl sulphate, and shaken at the ordinary temperature for one day, when the methosulphate separated. This salt was dissolved in water and treated with concentrated aqueous potassium bromide or any other soluble bromide, when the required methobromide was precipitated.

*Morphine ethobromide* was obtained from the corresponding ethiodide by treating the latter with moist silver bromide; it crystallises from water or alcohol in colourless needles melting at 245°. These quaternary salts have the narcotic action of morphine, but are far less poisonous.

G. T. M.

**The Alkyl Bromides of the Alkyl Ethers of Morphine.** J. D. RIEDEL (D.R.-P. 166362).—*Codeine methobromide*,  $C_{19}H_{24}O_3NBr$ , which is a white, crystalline powder melting at 261°, can be obtained by any of the following processes: from codeine and methyl bromide in dry chloroform, alcoholic, or acetone solution; by double decomposition from the methosulphate and lead bromide; by the methylation of morphine methobromide with sodium ethoxide and methyl bromide.

*Codeine ethobromide*,  $C_{20}H_{26}O_3NBr$ , produced from the corresponding ethiodide by the action of moist silver bromide, crystallises from acetone in lustrous needles, which contain acetone of crystallisation; these sinter at 70° and melt at 74°. When dried at 100–120°, the substance loses acetone, and then melts at 244–245°.

*Codethyline methobromide*,  $C_{20}H_{26}O_3NBr \cdot H_2O$ , is obtained either by evaporating a solution of codethyline methylammonium hydroxide with hydrobromic acid or by treating the methochloride (obtained either from the iodide with moist silver chloride or from the methosulphate with potassium chloride) with saturated aqueous potassium bromide; it crystallises in needles, which, after drying at 120°, melt at 267–268°.

*Codethyline ethobromide*,  $C_{21}H_{28}O_3NBr$ , produced by ethylating morphine at 80° with ethyl bromide and alcoholic potash, crystallises in soft, lustrous needles containing 3 or 4  $H_2O$ ; after dehydrating, it melts at 225°.

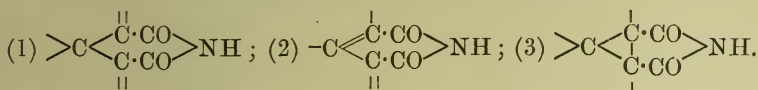
G. T. M.

**Products of Hydrogenation of Pyrrole by means of Reduced Nickel.** MAURIZIO PADOA (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 219–223).—By passing a mixture of pyrrole vapour and hydrogen



through a tube containing reduced nickel (from the reduction of nickel carbonate in hydrogen at 350°) at 180—190°, the author obtains: (1) a 25 per cent. yield of pyrrolidine, and (2) a small quantity of a hexahydroindoline (?), which gives a *picrate*,  $C_8H_{15}N, C_6H_3O_7N_3$ , crystallising from alcohol in yellow needles melting at 123°. T. H. P.

**Invertive Power of Certain Pseudo-acids having Complex Functions.** RODOLFO TORRESE (*Atti R. Accad. Sci. Torino*, 1906, 41, 309—327).—The author has examined, with regard to their capability of hydrolysing sucrose, a number of derivatives of glutaconimide having formulæ represented by the following schemes:

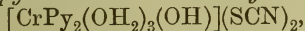


Compounds of types (1) and (3) are unable to hydrolyse sucrose, whilst those of type (2) are able to do so. In order, therefore, that they may exhibit this property, the molecules must possess a double linking in the position shown in (2), and they must, further, have the two carbonyl groups unsubstituted; if, for instance, one of the carbonyl groups is replaced by  $CMe_2$ , the power to invert sucrose is lost.

T. H. P.

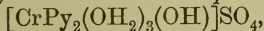
**A New Class of Salt-forming Metallic Hydroxides.** PAUL PFEIFFER [with M. TAPUACH and W. OSANN] (*Ber.*, 1906, 39, 1864—1879. Compare *Abstr.*, 1902, i, 728).—*Dihydroxylodiaquodipyridinechromium bromide*,  $[CrPy_2(OH_2)_2(OH)_2]Br$  (where  $Py = C_5NH_5$ ), is prepared by the addition of pyridine or of ammonia to an aqueous solution of the tetra-aquobromide,  $[CrPy_2(OH_2)_4]Br_3$  (*loc. cit.*).

*Hydroxylotriaquodipyridinechromium thiocyanate*,



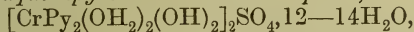
prepared from ammonium thiocyanate and tetra-aquodipyridinechromium chloride, forms violet-red crystals; its aqueous solution is greyish-green.

*Hydroxylotriaquodipyridinechromium sulphate*,



prepared by the addition of pyridine or of ammonia to an aqueous solution of the hydrogen sulphate,  $[CrPy_2(OH_2)_4](SO_4)_2H$ , forms a green solution with an excess of water.

*Dihydroxylodiaquodipyridinechromium sulphate*,



prepared by the action of ammonia on tetra-aquodipyridinechromium sulphate, forms greyish-violet crystals. It may also be formed from the trihydroxylo-compound by the careful addition of sulphuric acid. When sulphuric acid is added in excess to dihydroxylodiaquodipyridinechromium sulphate, the latter is converted into the monohydroxylo-sulphate, which then passes into the hydrogen tetra-aquosulphate. When an aqueous solution of dihydroxylodiaquodipyridinechromium sulphate is decomposed by ammonia, the trihydroxylo-compound is formed.



*Chromiumtrihydroxyloaquodipyridine*,  $[\text{CrPy}_2(\text{OH})_2(\text{OH})_3] \cdot 6\text{H}_2\text{O}$ , prepared by the action of concentrated ammonia on the dihydroxylo-sulphate or by the action of concentrated ammonia on the monohydroxylosulphate, or by the action of ammonia on a mixture of the dihydroxylochloride and the dihydroxylobromide suspended in water, forms glistening, violet crystals and is insoluble in water. It forms red solutions with dilute mineral acids.

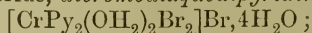
The corresponding dihydroxylo-salts are produced by the action of a little hydrochloric, hydrobromic, or sulphuric acid on an aqueous emulsion of the trihydroxyl compound in question. By the action of an excess of concentrated hydrochloric acid on the trihydroxyl compound, tetra-aquodipyridinechromium chloride is formed. Chromiumtrihydroxyloaquodipyridine is very unstable, undergoing partial decomposition when exposed to air at the ordinary temperature. A green residue is left when the compound is exposed in a desiccator containing phosphoric oxide or when it is kept under diminished pressure, water and pyridine being evolved in each case.

*Chromiumdichlorohydroxyloaquodipyridine*,  $[\text{CrPy}_2(\text{OH})_2(\text{OH})\text{Cl}_2]$ , was prepared as follows. The green product obtained by heating tetra-aquodipyridinechromium chloride in a sealed tube (compare succeeding abstract) was triturated with dilute hydrochloric acid, and to the solution remaining after filtration from chromiumtrichloro-aquodipyridine pyridine was probably added, when chromiumdichlorohydroxyloaquodipyridine was precipitated. It is a green microcrystalline powder which decomposes on prolonged exposure to the air at the ordinary temperature and is insoluble in water. Its solutions in dilute mineral acids are green. When suspended in water and ammonia then added, it forms the compound,  $[\text{CrPy}_2(\text{OH})_2(\text{OH})_2]\text{Cl}$ , which, by the action of concentrated hydrochloric acid, is converted into tetra-aquodipyridinechromium chloride,  $[\text{CrPy}_2(\text{OH})_2] \cdot 2\text{H}_2\text{O}$ .

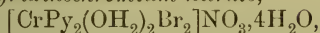
The constitution of the substances enumerated is discussed. The hydroxy-groupings are directly attached to the chromium atom. The compounds described form salts with acids by direct addition and not by substitution.

A. McK.

**Hydrate Isomerism with Chromium Salts.** PAUL PFEIFFER [and M. TAPUACH] (*Ber.*, 1906, 38, 1879—1896).—When the violet-red tetra-aquodipyridinechromium bromide,  $[\text{CrPy}_2(\text{OH})_2] \cdot \text{Br}_2 \cdot 2\text{H}_2\text{O}$ , where  $\text{Py} = \text{C}_5\text{NH}_5$  (compare Abstr., 1902, i, 728), is allowed to remain for several weeks in a closed vessel, it assumes a green tint. When heated in a closed vessel for three hours at  $60-65^\circ$ , it is converted into the green isomeride, *dibromodiaquodipyridinechromium bromide*,



the latter forms a green solution with ethyl alcohol or methyl alcohol. As distinguished from the violet-red isomeride, it does not form a clear solution with water, since it undergoes hydrolytic dissociation with the separation of a green powder (possibly  $[\text{CrPy}_2(\text{OH})_2(\text{OH})\text{Br}_2]$ ). When an excess of pyridine is added to a solution of the dibromobromide in water containing hydrochloric acid, a green precipitate of the pseudo-base,  $[\text{CrPy}_2(\text{OH})_2(\text{OH})\text{Br}_2]$ , is formed; the latter is very labile and is quickly transformed into the basic bromide of the tetra-aquo-series.

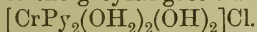
*Dibromodiaquodipyridinechromium nitrate,*

prepared from nitric acid and dibromodiaquodipyridinechromium bromide, forms dark green needles. It does not form a clear solution with water owing to partial separation of the hydroxydibromo-compound, which can be dissolved by the addition of mineral acid. When the dibromo-nitrate is added to water, the concentration of bromine ions in the solution remaining after filtration of the hydroxydibromo-compound is slight. The compound  $[\text{CrPy}_2(\text{OH}_2)_2\text{Br}_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$  may also be obtained as a bright green, microcrystalline powder by varying the conditions of the interaction between nitric acid and dibromodiaquodipyridinechromium bromide.

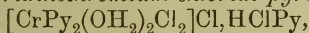
*Dibromodiaquodipyridinechromium iodide,*  $[\text{CrPy}_2(\text{OH}_2)_2\text{Br}_2]\text{I} \cdot 4\text{H}_2\text{O}$ ,

prepared by the addition of ammonium iodide to a solution of dibromodiaquodipyridinechromium bromide in hydrochloric acid, separates in dark green needles; its aqueous solution is turbid, on account of the formation by hydrolytic dissociation of a precipitate, probably consisting of the compound  $[\text{CrPy}_2(\text{OH}_2)(\text{OH})\text{Br}_2]$ ; the solution in dilute acids is green. When the salt is heated, iodine is evolved.

*Chromium trichloro-aquodipyridine,*  $[\text{CrPy}_2(\text{OH}_2)\text{Cl}_3] \cdot \text{H}_2\text{O}$ , prepared by heating the violet-red variety of tetra-aquopyridine chromium chloride,  $[\text{CrPy}_2(\text{OH}_2)_4]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , at  $75^\circ$ , and then washing the residue with hydrochloric acid until the filtrate is no longer green, is a yellowish-green powder. In the aqueous solution of the compound, the chlorine is not in the ionic form. When agitated with water and pyridine, the compound is transformed into the greyish-green dihydroxylochloride,

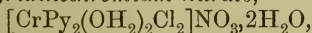


It may also be transformed into the isomeric dichloro-chloride,

*Dichlorodiaquodipyridinechromium chloride pyridinium chloride,*

obtained as a by-product in the preparation of chromiumtrichloro-aquodipyridine, forms glistening, green needles.

*Dichlorodiaquodipyridinechromium chloride,*  $[\text{CrPy}_2(\text{OH}_2)_2\text{Cl}_2]\text{Cl}$ , prepared by the action of concentrated hydrochloric acid on chromiumdichlorohydroxyloaquodipyridine (compare preceding abstract), forms glistening, green leaflets; it undergoes hydrolytic dissociation with formation of chromiumdichlorohydroxyloaquodipyridine. When exposed at the ordinary temperature, the crystals lose their lustre and hydrogen chloride is evolved.

*Dichlorodiaquodipyridinechromium nitrate,*

prepared by the action of concentrated nitric acid on chromiumdichlorohydroxyloaquodipyridine, forms green needles. In the aqueous solution of the compound, the chlorine is not in the ionic condition.

*Dichlorodiaquodipyridinechromium bromide,*  $[\text{CrPy}_2(\text{OH}_2)_2\text{Cl}_2]\text{Br} \cdot 3\text{H}_2\text{O}$ , prepared by the action of hydrobromic acid on chromiumdichlorohydroxyloaquodipyridine, forms dark green, prismatic needles.

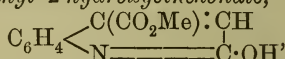
The constitution of these compounds, which are interesting types of isomerism, comparable with Werner's chromium bromide hexahydrates,  $[\text{Cr}(\text{OH}_2)_6]\text{Br}_3$  and  $[\text{Cr}(\text{OH}_2)_4\text{Br}_2]\text{Br} \cdot 2\text{H}_2\text{O}$ , is discussed in the preface.

A. McK.

**Preparation of Indoxyl and its Homologues.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 166213, 166214).—A mixture of potassium phenylglycinate, sodium and potassium hydroxides, and magnesium nitride is heated at 220—270° until the fused mass assumes a deep orange or brown colour. The product, when dissolved in water, filtered from magnesium hydroxide, and oxidised, gives a good yield of indigotin.

The phenylglycine employed in this reaction may be replaced by one of its homologues, and any other nitride of the alkaline earths may be substituted for the magnesium compound. A similar result is obtained when calcium carbide or any other alkali or alkaline-earth carbide is employed instead of the nitride. G. T. M.

**3-Ethylcinchonic Acid and 2-Hydroxy-3-ethylcinchonic Acid.** B. MULERT (*Ber.*, 1906, 39, 1901—1908. Compare Hübner, this vol., i, 383).—*Methyl 2-hydroxycinchonate*,



prepared by the action of hydrogen chloride on a solution of 2-hydroxycinchonic acid in methyl alcohol, melts at 245°. The corresponding

*amide*,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{C}(\text{CO} \cdot \text{NH}_2) \cdot \text{CH} \\ \text{N} \text{=====} \text{C} \cdot \text{OH} \end{array}$ , melts at 357—358°.

*2-Chlorocinchonyl chloride*,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{C}(\text{CO} \cdot \text{Cl}) \cdot \text{CH} \\ \text{N} \text{=====} \text{CCl} \end{array}$ , prepared by the action of thionyl chloride on 2-hydroxycinchonic acid, melts at 89—90° and is very stable towards cold water.

*2-Chlorocinchonamide*,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{C}(\text{CO} \cdot \text{NH}_2) \cdot \text{CH} \\ \text{N} \text{=====} \text{CCl} \end{array}$ , separates from dilute alcohol in prismatic needles and melts at 234—235°; on further heating it solidifies and again melts at 276—278°.

*2-Chlorocinchonanilide*,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{C}(\text{CO} \cdot \text{NHPh}) \cdot \text{CH} \\ \text{N} \text{=====} \text{CCl} \end{array}$ , separates from alcohol in needles and melts at 202°.

*Methyl 2-chlorocinchonate*,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{C}(\text{CO}_2\text{Me}) \cdot \text{CH} \\ \text{N} \text{=====} \text{CCl} \end{array}$ , prepared by the addition of 2-chlorocinchonyl chloride to methyl alcohol, melts at 89—90°.

*2-Methoxycinchonic acid*,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{C}(\text{CO}_2\text{H}) \cdot \text{CH} \\ \text{N} \text{=====} \text{C} \cdot \text{OMe} \end{array}$ , prepared by the action of sodium methoxide on 2-chlorocinchonic acid, separates from benzene in needles and melts at 178—179°. When heated above its melting point, it is transformed into the isomeric methyl 2-hydroxycinchonate melting at 245—255°. Its *methyl* ester separates from alcohol in needles and melts at 71°.

*3-Ethylcinchonic acid*,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{C}(\text{CO}_2\text{H}) \cdot \text{CEt} \\ \text{N} \text{=====} \text{CH} \end{array}$ , prepared by the condensation of isatin with butaldoxime in the presence of potassium hydroxide, melts at 222°. Its *sodium* and *silver* salts and its *platinichloride*

were prepared. Its *methyl betaine*,  $C_{13}H_{13}O_2N$ , prepared by the action of methyl iodide on the silver salt, crystallises in needles and melts at  $261^\circ$ .

*3-Ethylcinchon chloride hydrochloride*,  $C_{12}H_{10}ONCl \cdot HCl$ , crystallises in needles and melts at  $174-175^\circ$ .

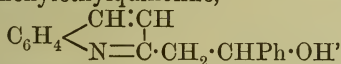
The *amide*,  $C_{12}H_{12}ON_2$ , separates from water in needles and melts at  $220-221^\circ$ . The *methyl ester*,  $C_{13}H_{13}O_2N$ , separates from ether in hexagonal prisms and melts at  $37-38^\circ$ .

*2-Hydroxy-3-ethylcinchon acid*,  $C_6H_4 \begin{smallmatrix} \text{C}(\text{CO}_2\text{H}) \cdot \text{CEt} \\ \text{N} = \text{C} \cdot \text{OH} \end{smallmatrix}$ , prepared from isatin and butyric anhydride in presence of aqueous sodium hydroxide, crystallises from water in needles and melts at  $285^\circ$ . Its *sodium* and *silver* salts are described. Its *acid chloride*, prepared by the action of thionyl chloride, separates from chloroform in plates and melts at  $194-195^\circ$ . Its *methyl ester* melts at  $160^\circ$ ; its *amide* melts at  $304-305^\circ$ .  
A. McK.

**Synthesis in Sunlight.** ALFRED BENRATH (*J. pr. Chem.*, 1906, [ii], 73, 383—389. Compare Klinger and Standke, *Abstr.*, 1891, 900; Klinger and Kolvenbach, *Abstr.*, 1898, i, 467).—When mixed with *isobutaldehyde*, *salicylaldehyde*, or *benzaldehyde*, and exposed to sunlight, benzil is reduced to benzilbenzoin; anisaldehyde has only a slight, whilst furfuraldehyde, cinnamaldehyde, and valeraldehyde have no reducing action on benzil in sunlight.

*1-Benzoyl-1:2-dihydroquinoline*,  $C_6H_4 \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{NBz} \cdot \text{CH}_2 \end{smallmatrix}$ , is formed when benzaldehyde and quinoline are exposed to sunlight; it crystallises in slender, white needles, melts at  $200^\circ$ , is not a base, and is hydrolysed by concentrated hydrochloric acid, forming benzoic acid and 1:2-dihydroquinoline (?); if it is hydrolysed with a hot alkali hydroxide solution, the resulting base is oxidised to quinoline.

*2-β-Hydroxy-β-phenylethylquinoline*,



formed in the same manner from benzaldehyde and 2-methylquinoline, crystallises from alcohol, melts at  $131^\circ$ , decomposes when heated, forming 2-styrylquinoline, water, 2-methylquinoline, and benzaldehyde, and when boiled with acetic anhydride yields 2-styrylquinoline. The *salts* are only sparingly soluble; the *nitrate* crystallises in yellow, feathery aggregates and melts at  $153^\circ$ ; the *platinichloride*,  $(C_{17}H_{15}ON)_2 \cdot H_2PtCl_6$ , melts at  $232^\circ$ .

The action of benzaldehyde on cinnamic acid in sunlight leads to the formation of αδ-dibenzoyl-βγ-diphenylbutane.

Benzaldehyde and pyridine do not interact when exposed to sunlight.  
G. Y.

**Chemical Nature of Methylene-azure.** AUGUST BERNTHSEN (*Ber.*, 1906, 39, 1804—1809).—The author discusses the constitution of methylene-azure, and confirms Kehrman's discovery that this substance is a mixture of di- and tri-methylthionine (this vol., i, 460).



*Diphenylaminesulphone*,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{SO}_2 \end{smallmatrix} C_6H_4$ , is produced when methyl-diphenylaminesulphone is heated with hydriodic acid, methyl iodide being formed quantitatively. It crystallises in long needles and melts at 257—259°. C. S.

**Condensation Products of Rhodanic Acid with Aldehydes.** GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 181—185. Compare this vol., i, 383).—Reduction of *o*-nitrobenzylidenerhodanic acid (Bondzyński, Abstr., 1887, 1108) by means of ferrous sulphate in ammoniacal solution yields *o*-aminobenzylidenerhodanic acid, which is deposited from aqueous alcohol in blood-red crystals, turning yellow at 200° and decomposing at 265—269°.

*m*-Nitrobenzylidenerhodanic acid,  $NO_2 \cdot C_6H_4 \cdot CH : C \begin{smallmatrix} \text{S} - \text{CS} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$ , prepared by the action of concentrated sulphuric acid on an alcoholic solution of rhodanic acid and *m*-nitrobenzaldehyde, crystallises from acetic acid in lemon-yellow needles melting and decomposing at 255° and is moderately soluble in benzene, ether, or chloroform, and readily so in alcohol, ethyl acetate, or acetone.

*p*-Dimethylaminobenzylidenerhodanic acid crystallises from alcohol in minute, blood-red needles, which begin to melt at 240° and are completely melted at about 270° (compare Andreaseh and Zipser, Abstr., 1905, i, 930).

*p*-isopropylbenzylidenerhodanic acid,  $C_{13}H_{13}ONS_2$ , prepared from cuminaldehyde and rhodanic acid, crystallises from aqueous alcohol in red needles melting at 154—157°, and is moderately soluble in benzene or ether and readily so in chloroform, acetic acid, or acetone.

4-Hydroxy-2-methyl-5-isopropylbenzylidenerhodanic acid,  $C_{14}H_{15}O_2NS_2$ , prepared from thymotic aldehyde and rhodanic acid, forms a mass of orange, woolly crystals melting at 220—221°, and dissolves readily in alcohol, ether, ethyl acetate, acetic acid, or acetone, and to a slight extent in benzene or chloroform.

Thymotic dialdehyde and rhodanic acid give the condensation product,  $OH \cdot C_6HMePr_\beta(CHO) \cdot CH : C \begin{smallmatrix} \text{S} - \text{CS} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$ , which crystallises from alcohol in yellow needles melting at 239—240° and is soluble in ether, ethyl acetate, acetone, or acetic acid, and to a slight extent in benzene.

$\beta$ -Hydroxynaphthaldehyde and rhodanic acid yield the compound  $OH \cdot C_{10}H_6 \cdot CH : C \begin{smallmatrix} \text{S} - \text{CS} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$ , which crystallises from aqueous alcohol in dark chestnut-red needles blackening at 210° and melting and decomposing at 220°, and dissolves readily in ether, benzene, chloroform, acetone, or acetic acid. T. H. P.

4:5-Diamino-2:6-dihydroxy-3-methylpyrimidine. EMANUEL MERCK (D.R.-P. 166267).—4:5-Diamino-2:6-dihydroxy-3-methylpyrimidine is readily obtained by dissolving 5-isonitroso-4-amino-2:6-

dihydroxy-3-methylpyrimidine in 60 per cent. sulphuric acid and electrolysing the solution in the cathode cell with leaden cathode and a current density of 3 amperes per sq. dm. The liquid is finally saturated with ammonia, when the diamine is set free in a very pure condition.

G. T. M.

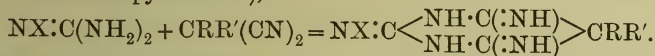
**Preparation of Cyclic Carbamide Derivatives (Pyrimidines).** EMANUEL MERCK (D.R.-P. 165561 and 165562).—Carbamide and its alkyl derivatives can be converted into pyrimidine bases by treatment with ethyl cyanoacetate in the presence of an alkali metal or its ethoxide or amide.

4-Amino-2 : 6-dioxypyrimidine,  $\text{CO} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{:NH}) \end{smallmatrix} \text{CH}_2$ , is prepared by the interaction of carbamide, sodamide, and ethyl cyanoacetate in xylene solution.

4-Ethylamino-2 : 6-dioxypyrimidine, obtained by condensing ethyl carbamide and ethyl cyanoacetate in the presence of sodium ethoxide, crystallises in fine needles and possesses both basic and acidic properties. The isonitroso-derivative of this base is a well-defined, violet-red substance melting indefinitely at 278—280°.

G. T. M.

**Preparation of Derivatives of Barbituric Acid.** EMANUEL MERCK (D.R.-P. 165692 and 165693).—Malononitrile and its mono- and di-*C*-alkylated homologues and guanidine and its derivatives undergo condensation to yield derivatives of tri-iminobarbituric acid (2 : 4 : 6-tri-iminopyrimidine),



These pyrimidine derivatives are readily hydrolysed to the corresponding barbituric acids, which have a distinctly soporific action.

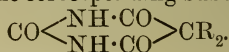
2 : 4 : 6-Tri-iminopyrimidine, melting at 252°, obtained from malononitrile and guanidine in alcoholic solution, yields sparingly soluble salts with the mineral acids and forms a violet nitroso-derivative. The compound from guanidine and ethylmalononitrile melts at 190°. 2 : 4 : 6-Tri-imino-5 : 5-diethylpyrimidine melts at 240° and has a strongly alkaline reaction. The compound from methylguanidine and diethylmalononitrile forms cubical crystals and melts at 172°. The compound  $\text{C}_9\text{H}_{14}\text{N}_6$ , obtained from diethylmalononitrile and either dicyanodiamide or diguanide, melts at 183°.

4 : 6-Di-imino-2-oxy-5-diethylpyrimidine, melting at 272°, obtained from carbamide and diethylmalononitrile, when boiled with 30 per cent. sulphuric acid yields diethylbarbituric acid. This substance may also be prepared from 2 : 4 : 6-tri-imino-5 : 5-diethylpyrimidine, melting at 240°, obtained by condensing diethylmalononitrile with guanidine.

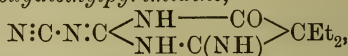
Ethylbarbituric acid (m. p. 194°) is prepared from 2 : 4 : 6-tri-imino-5-diethylpyrimidine, melting at 190°, and propylbarbituric acid may be produced from 4 : 6-di-imino-2-oxy-5-propylpyrimidine, which decomposes at 300° and is prepared from propylmalononitrile and carbamide in the presence of boiling alcoholic sodium ethoxide.

G. T. M.

**Preparation of 5:5-Dialkylbarbituric Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 165223).—By the action of dicyanodiamide on dialkylated cyanoacetates, malonates, or dialkylmalononitriles in the presence of alkaline condensing agents, pyrimidine derivatives are produced having the following general formula,  $N:C:N:C \begin{smallmatrix} \text{NH} \cdot \text{C}(:\text{X}) \\ \text{NH} \cdot \text{C}(:\text{X}) \end{smallmatrix} > \text{CR}_2$ , where R represents alkyl groups and X signifies oxygen atoms or imino-groups. These substances on treatment with acids furnish the corresponding substituted barbituric acids,



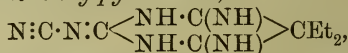
*Iminocyanoimino-oxydiethylpyrimidine,*



prepared from dicyanodiamide and ethyl diethylcyanoacetate in presence of an alkali ethoxide, separates from water in needles melting at 265° and yields diethylbarbituric acid on boiling with 20 per cent. sulphuric or oxalic acid.

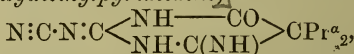
*Cyanoiminodioxydiethylpyrimidine,*  $N:C:N:C \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > \text{CEt}_2$ , from dicyanodiamide, ethyl diethylmalonate, and alkali ethoxide, melts at 242° and is readily hydrolysed by 25 per cent. hydrochloric acid.

*Di-iminocyanoiminodiethylpyrimidine,*



obtained from dicyanodiamide and diethylmalononitrile, melts at 270°.

*[Iminocyanoimino-oxydiethylpyrimidine,]*



arising from ethyl dipropylcyanoacetate, melts at 272°, and when hydrolysed with 25 per cent. hydrobromic acid yields 5:5-dipropylbarbituric acid. G. T. M.

**Preparation of 5:5-Dialkylbarbituric Acids.** ALFRED EINHORN (D.R.-P. 165649).—The 5:5-dialkylbarbituric acids may be obtained from the corresponding thiobarbituric acids by heating with non-oxidising mineral acids. After six to seven hours' boiling with concentrated hydrobromic acid or 33—50 per cent. sulphuric acid, diethylthiobarbituric acid is hydrolysed and dissolved, and pure 5:5-diethylbarbituric acid may be isolated from the product. Hydriodic, hydrochloric, sulphurous, and phosphoric acids may also be employed, and the hydrolysis is accelerated by the addition of alcohol. G. T. M.

**Preparation of 2-Arylimino- and 2-Arylhydrazino-5:5-dialkylbarbituric Acids.** ALFRED EINHORN (D.R.-P. 166266).—When the thiodialkylbarbituric acids are heated with aromatic amines, sulphur is displaced by the amino-residues and aryliminodialkylbarbituric acids are obtained.

*2-Phenyliminodiethylbarbituric acid*, which results from the interaction of aniline and thiodiethylbarbituric acid at 120—130°, crystallises from alcohol in white needles or leaflets melting at 253°; when



boiled with mineral acids, it is hydrolysed, yielding aniline and diethylbarbituric acid.

*2-Phenylhydrazinodiethylbarbituric acid*, obtained under similar conditions from thiodiethylbarbituric acid and phenylhydrazine, is sparingly soluble in methyl and ethyl alcohols, crystallising from the former in yellow leaflets melting at  $215-216^{\circ}$ ; it dissolves in dilute aqueous sodium hydroxide, and the solution passes through a series of colour changes—brown, reddish-brown, deep violet, and finally brown again; the liquid at the same time gradually becomes turbid. This hydrazino-derivative is hydrolysed by concentrated mineral acids, phenylhydrazine being eliminated.

*2-Phenyliminodimethylbarbituric acid* crystallises from alcohol in needles melting at  $251^{\circ}$ .  
G. T. M.

**Affinity Constants of Cyclic Bases.** GEORG DEDICHEN (*Ber.*, 1906, 39, 1831—1856).—The dissociation constants have been determined of substituted glyoxalines by the conductivity method, of derivatives of pyrazole, triazole, and of isodihydrotetrazine by Lowenherz's solubility process, or by the hydrolysis of ethyl formate.

The original paper must be consulted for the tabulated results. In general, the introduction of the methyl or ethyl group affects the affinity of the base to approximately the same extent. The position of the alkyl group has a very marked influence; when it is attached to a nitrogen atom, the effect on the dissociation constant is small, but the affinity of the base is largely increased when an alkyl group is combined with carbon. The introduction of a chlorine atom into 1-methylglyoxaline greatly diminishes the value of  $K$ .  
C. S.

**Resolution of the Iminazole and Oxazole Rings.** OTTO FISCHER (*J. pr. Chem.*, 1906, [ii], 73, 419—446. Compare Abstr., 1905, i, 245).—[With FRITZ RÖMER].—1-Methyl-, 1-ethyl-, and 1-phenylbenziminazoles are not reduced by sodium and alcohol.

The action of methyl iodide on 2:5-dimethylbenziminazole leads to the formation of 1:2:3:6-tetramethylbenziminazolium iodide and the hydriodides of 1:2:5- and 1:2:6-trimethylbenziminazoles (Fischer and Rigaud, Abstr., 1902, i, 399).

1:2:3:6-Tetramethyl-2:3-dihydrobenziminazole-2-ol (Fischer and Rigaud, *loc. cit.*) sublimes and decomposes only slightly when carefully heated, but decomposes to a marked extent when rapidly heated or distilled. It crystallises from light petroleum in sheaves of needles melting at  $148-150^{\circ}$ , or from water or very dilute alcohol in plates melting at  $166-167^{\circ}$ , and distils only slowly in a current of steam. It dissolves in cold acids, and can be reprecipitated immediately by alkali hydroxides or ammonia, but in the acid solution gradually changes into the benziminazolium salt, and is no longer precipitated by ammonia. 1:2:3:6-Tetramethylbenziminazolium picrate melts at  $147-148^{\circ}$  (compare Niementowski, Abstr., 1887, 937). The *nitroso-amine*,  $\text{NO} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NMeAc}$ , is formed by the action of sodium nitrite on 1:2:3:6-tetramethyldihydrobenziminazole-2-ol in concentrated sulphuric acid solution at  $0^{\circ}$ : it crystallises from a mixture of alcohol and light petroleum in long, stout, colourless prisms, melts



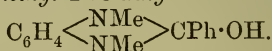
at 71°, becomes yellow or brown in presence of moisture, and gives Liebermann's reaction. The action of alcoholic hydrochloric acid on the nitrosoamine in ethereal solution leads to the formation of 1:2:3:6-tetramethylbenziminazolium chloride.

When heated with sodium hydroxide in alcoholic solution in a sealed tube at 150°, the carbinol or 1:2:3:6-tetramethylbenziminazolium iodide is decomposed, forming 3:4-dimethylaminotoluene, the hydrochloride of which has the formula  $C_9H_{16}N_2Cl_2$  (compare Fischer and Rigaud, *loc. cit.*).

The reduction of the carbinol with sodium and alcohol or zinc dust in alkaline solution leads to the formation of 1:2:3:6-tetramethyl-2:3-dihydrobenziminazole,  $C_6H_3Me<\begin{smallmatrix} NMe \\ NMe \end{smallmatrix}>CHMe$ , which is readily hydrolysed, yielding acetaldehyde and 3:4-dimethylaminotoluene.

When reduced with sodium and alcohol, 1:3:4:6-tetramethyldihydrobenziminazole-2-ol yields formaldehyde and *m*-xylylene-4:5-dimethyldiamine,  $C_6H_2Me_2(NHMe)_2$ . This is obtained as an oil, which boils at 245—250° under 730 mm. pressure, gives with ferric chloride in dilute solution a brownish-red coloration, or in concentrated hydrochloric acid solution a yellow *ferrichloride*, gradually changing into the red *azine* dye, and reacts with formic acid to form 1:3:4:6-tetramethyldihydrobenziminazole-2-ol, or with aldehydes to form unstable dihydrobenziminazoles. The *hydrochloride*,  $C_{10}H_{16}N_2 \cdot 2HCl$ , crystallises in white, flat prisms. When mixed with salicylaldehyde, the base forms water, and the *condensation product*,  $C_{17}H_{20}ON_2$ , which crystallises from ether in colourless plates, melts at 132—133° and is hydrolysed to salicylaldehyde and the *o*-diamine when boiled with acids.

2-Phenyl-1:3-dimethylbenziminazolium iodide,  $C_{15}H_{15}N_2I$ , formed by heating 2-phenylbenziminazole with methyl iodide and methyl alcohol in a sealed tube at 110°, crystallises in white needles, melts at 278—279°, and, when treated with a hot aqueous alkali hydroxide, forms 2-phenyl-1:3-dimethyl-2:3-dihydrobenziminazole-2-ol,



This crystallises in white, tetragonal prisms, melts at 159°, forms a *ferrichloride*, which is readily soluble in water, and with hydriodic acid yields the above benziminazolium iodide, or with alcoholic hydrochloric acid the *chloride*,  $C_{15}H_{15}N_2Cl$ . When dissolved in dilute hydrochloric acid, cooled by ice, and immediately treated with ammonia, 2-phenyl-1:3-dimethyldihydrobenziminazole-2-ol is regained unchanged, but after twenty to thirty minutes in the acid solution it is converted into the benziminazolium salt, which does not give a precipitate with ammonia. The *picrate* of the carbinol melts at 157—158°. When boiled with alcoholic potassium hydroxide, the carbinol is decomposed and forms *o*-phenylenedimethyldiamine.

2-Methyl-*a*-naphthiminazole melts at 171—172° (168—169°; Abstr., 1901, i, 414); when heated with methyl iodide and methyl alcohol in a sealed tube at 140—145°, it forms 1:2:3-trimethyl-*a*-naphthiminazolium iodide,  $C_{14}H_{15}N_2I$ , which crystallises in voluminous, white needles, becomes red when dried, melts at 294°, and when treated with aqueous-alcoholic potassium hydroxide yields the *carbinol*,

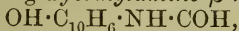
$C_{10}H_6 \begin{smallmatrix} \text{NMe} \\ \text{NMe} \end{smallmatrix} > CMe \cdot OH$ . This crystallises in white, tetragonal prisms, is readily soluble in alcohol, ether, or benzene, forming a solution with violet fluorescence, yields a yellow, crystalline *ferrichloride*, and is converted by acids slowly into the naphthiminazolium salts. The carbinol is very stable towards hydrolysing agents, remaining unchanged when heated with 50 per cent. alcoholic potassium hydroxide at 140—150°, and does not form an azine dye when treated with ferric chloride. The *nitrosoamine*, which is obtained in small yields when the carbinol is treated with sodium nitrite and dilute sulphuric acid cooled by ice, crystallises in slightly yellow plates, melts at 134—135°, and gives Liebermann's reaction.

When heated with methyl iodide and methyl alcohol at 120° in a sealed tube, benzoxazole forms *o*-trimethylaminophenol iodide (Griess, Abstr., 1880, 636). *Benzoxazole methiodide*,  $C_6H_4 \begin{smallmatrix} \text{N(MeI)} \\ \text{O} \end{smallmatrix} > CH$ , is formed when benzoxazole is heated with an excess of methyl iodide, without methyl alcohol, in a sealed tube at 100°; it crystallises in glistening, yellow needles, melts and evolves iodine at 182—183°, and decomposes when exposed to sunlight. When boiled with concentrated hydrochloric acid, the methiodide is hydrolysed, forming *o*-methylaminophenol.

When heated with methyl iodide at 170°, 2-phenylbenzoxazole yields only a small amount of an impure product containing iodine. Contrary to Hübner's statement (Abstr., 1882, 505), the product of the nitration of 2-phenylbenzoxazole is a *mononitro*-derivative, which, when hydrolysed with concentrated hydrochloric acid, yields benzoic acid. The *picrate*,  $C_{13}H_9ON, C_6H_3O_7N_3$ , crystallises in matted, yellow needles and melts at 104°.

*$\alpha$ -Naphthoxazole*,  $CH \begin{smallmatrix} C_6H_4 \cdot C \cdot N \\ | \\ CH - C \cdot O \end{smallmatrix} > CH$ , is prepared by heating

*$\alpha$ -amino- $\beta$ -naphthol* hydrochloride with sodium formate and formic acid in a reflux apparatus; it crystallises in white leaflets, melts at 63·5—64°, and is partially hydrolysed when heated with an aqueous alkali hydroxide. The *platinichloride* is unstable; the *mercurichloride*,  $C_{11}H_7ON, HgCl_2$ , crystallises in long, colourless, glistening needles and melts at 183—184°; the *picrate*,  $C_{11}H_7ON, C_6H_3O_7N_3$ , forms needles and melts at 133—134°. The *mononitro*-product,  $C_{11}H_6O_3N_2$ , formed by the action of cold nitric and sulphuric acids on  *$\alpha$ -naphthoxazole*, crystallises in brownish-yellow needles and melts at 135°. When boiled with water in a reflux apparatus for four hours,  *$\alpha$ -naphthoxazole* is hydrolysed, yielding  *$\alpha$ -formylamino- $\beta$ -naphthol*,



which crystallises in white, prismatic needles, melts at 204°, and is hydrolysed by boiling concentrated alkali hydroxides, yielding ammonia and  *$\alpha\beta$ -dihydroxynaphthalene*. When oxidised with chromic acid in glacial acetic acid solution,  *$\alpha$ -naphthoxazole* yields a small amount of an *o*-dicarboxylic acid.

*$\beta$ -Naphthoxazole*,  $C_{11}H_7ON$ , prepared from  *$\beta$ -amino- $\alpha$ -naphthol*, crystallises in stellate groups of slender needles, melts at 79° and is

hydrolysed to only a slight extent by boiling water. When boiled with dilute hydrochloric acid, it is decomposed, forming imino-oxydihydronaphthalene on saturating the solution with ammonia. When boiled with dilute potassium hydroxide, it yields ammonia and  $\alpha\beta$ -dihydroxynaphthalene.

Triphenylglyoxaline [lophine], when heated with methyl iodide and methyl alcohol at 120—130°, forms *triphenyldimethylglyoxalinium iodide*,  $C_{23}H_{21}N_2I$ , which separates from alcohol in white crystals, melts at 266°, and remains unchanged when treated with alcoholic potassium hydroxide. When reduced with sodium and alcohol, it yields benzoic acid, methylamine, and *s-dimethylstilbenediamine*,  $C_{16}H_{20}N_2$ , which is formed also by hydrolysis of *i*-benzoyl-*s*-dimethylstilbenediamine (Japp and Moir, *Trans.*, 1900, 77, 608) with concentrated hydrochloric acid at 170—180°. The *hydrochloride* of the diamine,  $C_{16}H_{20}N_2 \cdot 2HCl$ , was analysed; the *aurichloride*, *platinichloride*, *mercurichloride*, and *picrate* are crystalline. The *dinitrosoamine*,  $C_{16}H_{18}O_2N_4$ , crystallises from acetone in almost colourless, tetragonal prisms, melts at 266—267°, and gives Liebermann's reaction.

The *diacetyl* derivative,  $C_{20}H_{24}O_2N_2$ , crystallises in white, nodular aggregates and melts at 250—251°. The *dibenzoyl* derivative,  $C_{30}H_{28}O_2N_2$ , melts at 248—250°.

The *nitroso*-derivative of *i*-benzoyl-*s*-dimethylstilbenediamine melts at 213—215°, and gives Liebermann's reaction. G. Y.

**Preparation of Indoxyl and its Derivatives.** BASLER CHEMISCHE FABRIK (D.R.-P. 165691).—A convenient process for obtaining indoxyl from phenylglycine consists in adding the potassium salt of the latter to an intimate mixture of potassium hydroxide and sodium oxide (prepared from the metal) heated at 210—260°. The fused mass from ten parts of the alkali phenylglycine derivative when dissolved in water and oxidised by a current of air yielded 4.8 parts of indigo. In this experiment, the phenylglycine may be replaced by its homologues, giving rise to the corresponding indoxyl derivatives.

G. T. M.

**Synthesis of Derivatives of Ketoquinazoline.** BRONISLAW VON PAWLEWSKI (*Ber.*, 1906, 39, 1732—1736. Compare *Abstr.*, 1905, i, 246; Kunckell, *Abstr.*, 1905, i, 382).—Anthranilic acid reacts with disubstituted carbamides or thiocarbamides to form only mono-substituted derivatives of ketotetrahydroquinazoline, in the sense of the equation  $NH_2 \cdot C_6H_4 \cdot CO_2H + NHR \cdot CO \cdot NHR' = C_6H_4 \begin{smallmatrix} \text{CO} - \text{NR} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} + H_2O + R'NH_2$ . Thus, phenylallylthiocarbamide forms 4-keto-2-thion-3-phenyl-1:2:3:4-tetrahydroquinazoline, allylamine, and water.

Molecular quantities of anthranilic acid and allyl thiocarbamide at 150—180° react to form 4-keto-2-thion-3-allyl-1:2:3:4-tetrahydroquinazoline,  $C_8H_4 \begin{smallmatrix} \text{CO} - \text{N} \cdot C_3H_5 \\ \text{NH} \cdot \text{CS} \end{smallmatrix}$ , which melts at 303—304°, and is

oxidised by hydrogen peroxide in alkaline solution to 2:4-diketo-3-allyl-1:2:3:4-tetrahydroquinazoline, which separates from alcohol in needles and melts at 276—278°.



4-Keto-2-thion-1-allyl-1:2:3:4-tetrahydroquinazoline is obtained when a mixture of anthranilic acid and allyl thiocarbimide is heated at 160—165° and finally at 170—180°. It crystallises from alcohol in long prisms, melts at 208—210°, and is oxidised by hydrogen peroxide to 2:4-diketo-1-allyl-1:2:3:4-tetrahydroquinazoline, which separates from alcohol in long, irregular leaflets and melts at 187—189°.

Anthranilic acid and *o*-tolylthiocarbimide react to form 4-keto-2-thion-3-*o*-tolyl-1:2:3:4-tetrahydroquinazoline (compare MacCoy, Abstr., 1897, i, 490; Freundler, Abstr., 1904, i, 830), which crystallises in colourless prisms and needles, melts at 270—271°, and is oxidised by hydrogen peroxide to Busch's 2:4-diketo-3-*o*-tolyl-1:2:3:4-tetrahydroquinazoline (Abstr., 1895, i, 307). C. S.

**Preparation of Diaminodinaphthazines.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 166363).—The dinaphthazines when dissolved in concentrated sulphuric acid readily yield dinitro-derivatives on nitration; these products on reduction give rise to diaminodinaphthazines, which furnish valuable azo-colouring matters. These diaminodinaphthazines, unlike the aminoazines already described, which contain the amino-group in the para-position, do not exchange this group for hydroxyl on heating under pressure with hydrochloric acid.

$\alpha\beta$ -Dinaphthazine furnishes a dinitro-derivative which is very sparingly soluble in all indifferent solvents and crystallises from nitrobenzene in small, yellow needles melting above 300°. This product is reduced to the corresponding *diamino- $\alpha\beta$ -dinaphthazine* by mixing intimately with concentrated sodium sulphide solution and heating the mixture at 90—100°. The diamine is a red substance melting above 300°; it is insoluble in water and sparingly soluble in all organic solvents; its *sulphate* separates from aqueous solutions in very sparingly soluble pale yellow crystals. The compounds obtained under these conditions from  $\beta\beta$ -dinaphthazine are quite analogous to the preceding substances. G. T. M.

**Condensation Reaction of the Pyrazolones.** MARIO BETTI and CURIO M. MUNDICI (*Gazzetta*, 1906, 36, i, 178—187).—Pyrazolone reacts with  $\beta$ -hydroxynaphthaldehyde, forming in the first place an unstable, intermediate compound,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CH} \left( \text{CH} \begin{smallmatrix} \text{CO-NPh} \\ \text{CMe:N} \end{smallmatrix} \right)_2$ , which readily decomposes, yielding methenylbisphenylmethylpyrazolone,  $\text{NPh} \cdot \text{CO} \begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{C} \\ \text{N} = \text{CMe} \end{smallmatrix} \begin{smallmatrix} \text{CO-NPh} \\ \text{CMe:N} \end{smallmatrix}$ . The reaction evidently depends on the known tendency of the pyrazolones to form the grouping  $\text{=CH} \cdot \text{CH} \cdot \text{C=}$ .  $\beta$ -Hydroxynaphthaldehyde does not react with methylisooxalazone or with partially substituted pyrazolones or with ethyl malonate; with aromatic amines, it yields anilides and hydrazones.

[Methylbisphenylmethylpyrazolone],  $\text{C}_{21}\text{H}_{18}\text{O}_2\text{N}_4$ , crystallises in shining, orange-yellow needles melting at 180°, and dissolves moderately well in alcohol and to a slight extent in other organic solvents. It is

See *supra*  
V. 90<sup>2</sup>, p. 1266



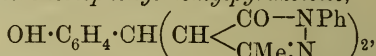
soluble in sodium hydroxide solution and in concentrated sulphuric acid, to which it imparts an intense yellow colour.

The intermediate compound, *β*-hydroxynaphthylidenebisphenylmethylpyrazolone,  $C_{31}H_{26}O_3N_4$ , separates in slender, yellow needles melting at  $118^\circ$  to a turbid, yellow liquid which becomes transparent at about  $140^\circ$ ; it cannot be purified, owing to its instability.

*Methenylbismethylpyrazolone*, 
$$\begin{array}{c} \text{NH}-\text{CO} \\ | \quad \diagup \\ \text{N}=\text{CMe} \end{array} > \text{CH} \cdot \text{CH} : \text{C} < \begin{array}{c} \text{CO}-\text{NH} \\ \diagdown \quad | \\ \text{CMe}=\text{N} \end{array}$$
, crystallises from alcohol with EtOH in golden-yellow needles melting at  $130-140^\circ$ , and dissolves in concentrated sulphuric acid giving a yellow coloration, and in sodium hydroxide solution forming an intensely yellow liquid.

*Methenylbisdiethylpyrazolone*, 
$$\begin{array}{c} \text{NPh} \cdot \text{CO} \\ | \quad \diagup \\ \text{N}=\text{CPh} \end{array} > \text{CH} \cdot \text{CH} : \text{C} < \begin{array}{c} \text{CO}-\text{NPh} \\ \diagdown \quad | \\ \text{CPh}=\text{N} \end{array}$$
, crystallises from alcohol in reddish-yellow needles and from benzene in orange-yellow needles melting at  $249-250^\circ$ .

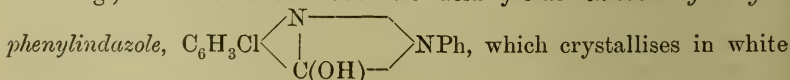
*o*-Hydroxybenzylidenebisphenylmethylpyrazolone,



prepared from salicylaldehyde and phenylmethylpyrazolone, crystallises from alcohol in colourless needles melting at  $228-230^\circ$ , dissolves but slightly in other organic solvents, forms a reddish-yellow solution with concentrated sulphuric acid, and dissolves in sodium hydroxide solution.

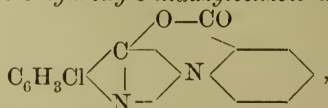
*Anisylidenebisphenylmethylpyrazolone*,  $C_{28}H_{25}O_3N_4$ , crystallises from alcohol in colourless needles which contain EtOH and melt at  $148^\circ$ , and dissolves in sodium hydroxide solution or concentrated sulphuric acid.  
T. H. P.

**Azo-compounds. Transformation of *o*-Carboxylic Azo-compounds into 3-Hydroxyindazyl Derivatives.** PAUL FREUNDLER (*Compt. rend.*, 1906, 142, 1153—1155.—Compare Abstr., 1903, i, 371, 585; 1904, i, 121, 667, 699).—Azo-compounds containing a carboxylic group in the *ortho*-position do not react normally with phosphorus pentachloride, but yield a 3-hydroxyindazyl derivative chlorinated in the ring; thus benzene-*o*-azobenzoic acid yields *chloro-3-hydroxy-2-phenylindazole*,  $C_6H_3Cl$



plates, melts at  $265^\circ$ , is soluble in acetic acid, and almost insoluble in benzene or chloroform, and yields *benzene-*o*-azochlorobenzoic acid*,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{N}_2 \cdot \text{Ph}$ , on oxidation with chromic acid or dilute nitric acid, which melts at  $124-125^\circ$ .

The lactone of *chloro-3-hydroxy-*o*-indazylbenzoic acid*,



obtained by decomposing with water the product of the action of phosphorus pentachloride on *o*-azobenzoic acid, forms thin needles which

melt at  $241^{\circ}$ , is soluble in benzene, and is converted by nitric acid into chlorodinitrobenzeneazobenzoic acid melting at  $225^{\circ}$ . M. A. W.

**Nitration of 2-Hydroxy-1-diazonaphthalene-4-sulphonic Acid.** ANILINFARBEN- & EXTRACT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 164665).—Well-dried powdered 2-hydroxy-1-diazonaphthalene-4-sulphonic acid dissolved in cold concentrated sulphuric acid was gradually treated at  $0-5^{\circ}$  with a mixture of concentrated nitric and sulphuric acids; the mixture was stirred for four hours, allowed to attain a temperature of  $15^{\circ}$ , and then poured on to ice, when *nitro-2-hydroxy-1-diazonaphthalene-4-sulphonic acid* separated in the form of pale yellow crystals, which can be dried at  $80-100^{\circ}$  and are not explosive. The new nitrodiazo-derivative, which is more soluble than the unnitrated compound, readily condenses with phenols to yield azo-colouring matters. G. T. M.

**The Electrical Charge of Proteid and its Significance.** WOLFGANG PAULI (*Chem. Centr.*, 1906, i, 376—377; from *Naturw. Rundsch.*, 21, 3—5, 17—20).—The serum proteids free from electrolytes have no electrical charge; addition of neutral salts leaves them unchanged, so also does alcohol, which precipitates them readily. Traces of acid or alkali confer on them a positive or negative charge respectively, and hinder their precipitability by alcohol. The differently charged proteids behave in a reverse manner to various ions. The naturally occurring proteids are electro-negative, and the electrical properties of cells and tissues are believed to depend on the charge in their proteid constituents. The similarity between the reactions of colloids and immune substances and between the reactions of the latter substances and fertilisation phenomena is pointed out.

W. D. H.

**Optical Rotation and Density of Alcoholic Solutions of Gliadin.** W. E. MATHEWSON (*J. Amer. Chem. Soc.*, 1906, 28, 624—628).—An investigation has been made of the variation in the specific rotatory power of gliadin with changes of temperature, concentration, and the nature of the solvent. It has been found that the specific rotation of a solution in 70—75 per cent. alcohol is practically independent of the concentration of the gliadin. Solutions of the proteid in 70—80 per cent. alcohol show a marked increase in specific rotation as the percentage of water in the solvent increases. A rise of temperature between  $20^{\circ}$  and  $45^{\circ}$  produces a slight increase in the specific rotation.

Fleurent (*Compt. rend.*, 1901, 132, 1421) has described a method for the estimation of gliadin in flours based on the sp. gr. of the alcoholic extract. It is now shown, however, that the differences in the sp. gr. in such cases are too small to afford accurate results.

E. G.

**The Amount of Glycine in Milk Proteids.** EMIL ARDERHALDEN and A. HUNTER (*Zeit. physiol. Chem.*, 1906, 47, 404—406).—Skraup

(this vol., i, 123) states that caseinogen contains glycine. This is not the case for the pure substance prepared by Hammarsten's process. The mixed coagulable proteids of milk (lactalbumin and lactoglobulin) yield a small quantity, 1.2 grams of glycine-hydrochloride from 100 grams of the proteid material. Whether this is derived from the albumin or globulin or both is not decided.

W. D. H.

**The Monoamino-acids of Legumin.** EMIL ABDERHALDEN and BORIS BABKIN (*Zeit. physiol. Chem.*, 1906, 47, 354—358. Compare this vol., i, 56).—Legumin prepared from white beans yields on hydrolysis: glycine, 1; alanine, 2.8; aminovaleric acid, 1; leucine, 8.2; pyrrolidine-2-carboxylic acid, 2.3; phenylalanine, 2; glutamic acid, 16.3; aspartic acid, 4; and tyrosine, 2.8 per cent. The numbers obtained resemble those obtained from conglutin. Conglutin yields 19.5 per cent. of glutamic acid; this corrects a previous statement of the authors, that the yield is low.

W. D. H.

**Physical Chemistry of Oxyhæmoglobin. The Capacity for Combining with Alkali of the Colouring Matter of Blood.** EMIL ABEL and OTTO VON FÜRTH (*Zeit. Elektrochem.*, 1906, 12, 349—359).—Sodium hydroxide is added to solutions of hæmoglobin, and the concentration of the hydroxyl ions in the resulting solution determined by means of a hydrogen electrode. By comparing the actual concentrations found with those calculated from the quantity of sodium hydroxide added, it is found that 51 mg. of sodium hydroxide are neutralised by one gram of hæmoglobin. The compound is hydrolysed to a considerable extent; if no excess of sodium hydroxide has been added, the hydrolysis amounts to about 18 per cent.

Similar experiments with oxyhæmoglobin were not very successful; the results were not sufficiently definite to admit of any calculation of the concentration of the hydroxyl ions.

T. E.

**Action of Quinine on Hæmoglobin.** HUGO MARX (*Chem. Centr.*, 1906, i, 1443; from *Arch. exp. Path. Pharm.*, 54, 460—464).—The addition of quinine to blood (fresh or dry) changes the colour to brown, and spectroscopically a well-marked band in the red is seen. Brown crystals separate out; similar results follow the action of quinine on aceto-hæmin crystals. If hæmatoporphyrin hydrochloride is dissolved in a concentrated solution of quinine, the latter substance is precipitated in a crystalline form which carries down the pigment with it.

W. D. H.

**Neuræmin.** GABLIN & CIE. (*Chem. Centr.*, 1906, i, 563; from *Pharm. Zeit.*, 1906, 51, 77).—*Neuræmin* is prepared by slowly adding a solution of 10 grams of hæmatin and 10 grams of smilacin in two litres of 90 per cent. alcohol to a solution of 20 grams of lecithin in 100 grams of ether; on distilling off the solvents in a vacuum at 30°, the neuræmin is obtained in the form of a reddish-brown, wax-like solid, which melts at 128° and is readily soluble in alcohol, ether, or acetone.

P. H.

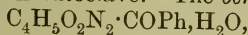


**The Cleavage Products of Spongin with Acids.** EMIL ABDERHALDEN and EDUARD STRAUSS (*Zeit. physiol. Chem.*, 1906, **48**, 49—53).—In many of the so-called albuminoids (using the term in the limited sense usual among physiologists), typical cleavage products are absent; for instance, tyrosine is absent from gelatin and spongin. Phenylalanine is absent from spongin and keratin. Pyrrolidine-2-carboxylic acid, glycine, and glutamic acid (in large quantities) are obtained from spongin. The transformation of ordinary proteids into such skeletal substances appears to be a result of metabolism and of the action of tissue enzymes.

W. D. H.

**Decomposition of Histidine.** SIGMUND FRÄNKEL (*Beitr. chem. Physiol. Path.*, 1906, **8**, 156—162. Compare Abstr., 1903, i, 650; Pauly, *ibid.*, 1904, i, 1068; Knoop and Windaus, *ibid.*, 1905, i, 834).—*Chlorohistidylcarboxylic acid*,  $C_6H_7O_2N_2Cl$ , is formed when histidine hydrochloride is treated with nitrous acid at  $0^\circ$ , and the syrup thus obtained reduced with zinc and acetic acid. It crystallises from water in long, transparent plates containing  $H_2O$  and melts at  $80^\circ$ . When reduced, it yields *histidylcarboxylic acid* in the form of small crystals, melting at  $195^\circ$  and readily soluble in water. When oxidised with dichromate and sulphuric acid, histidine yields acetic acid and hydrogen cyanide, and when heated at  $220^\circ$  with 20 per cent. hydrochloric acid it yields racemic histidine hydrochloride melting at  $220^\circ$ . When benzoylated by the Schotten-Baumann method, histidine yields a *monobenzoyl* derivative which melts and decomposes at  $230^\circ$ . Even when a large excess of benzoyl chloride is used, no rupture of the ring occurs, and this is regarded as a strong argument against the iminazole formula suggested by Pauly (compare Bamberger and Berlé, Abstr., 1892, 632). *Histidylcarboxylic acid* cannot be benzoylated. When the hydrochloride of the base is heated above its melting point, carbon dioxide is evolved and a small amount of a compound,  $C_4H_6O_2N_2$ , can be isolated. Fuming nitric acid reacts with histidine, yielding a yellow, crystalline compound containing water of crystallisation. The anhydrous compound has the composition  $C_4H_7O_5N_3$ .

Formic acid and a compound,  $C_4H_6O_2N_2 \cdot 2H_2O$ , which melts at  $247^\circ$  when anhydrous, are formed when histidine is heated with barium hydroxide and water in an autoclave. The *benzoyl* derivative,



melts at  $225^\circ$ .

J. J. S.

**Diastatic Saccharification.** LÉON MAQUENNE and EUGÈNE ROUX (*Compt. rend.*, 1906, **142**, 1059—1065. Compare this vol., i, 327).—Further experiments on the action of amylase on starch mucilage show that the optimum condition (slightly alkaline liquid) for the production of dextrin is also that which ensures the largest yield of maltose. In a neutral liquid, more maltose may be produced at first, but the reaction stops sooner and the amount of maltose ultimately produced is smaller.

Crude starch contains two products, one readily attacked by amylase and the other (amylopectin) more resistant, but it is also eventually converted into maltose by the enzyme. The neutralisation of amylase



solutions by acids diminishes the stability of the enzyme. The addition of small quantities of acid to starch mucilage undergoing hydrolysis by amylase accelerates the production of maltose, but the addition of further quantities diminishes the activity. Hence it appears probable that amylase occurs in its solutions in combination with a mineral or amino-base forming a kind of zymogen more stable than amylase itself, and that it is liberated from the zymogen by the addition of small quantities of acid.

Solutions of amylase which have been partially neutralised by acid frequently show a change in reaction as saccharification proceeds and tend to revert to the original alkaline condition. The alkali probably results from the decomposition of proteids in the amylase solution by proteolytic enzymes.

T. A. H.

**Influence of Chemical Constitution on the Lipolytic Hydrolysis of Esters.** JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1536—1537; from *Public Health and Marine-Hospital Service of U.S. Hygienic Lab. Bull.* No. 26, 43—51).—Experiments show that whilst the methyl, ethyl, butyl, isobutyl, allyl, and benzyl groups have almost the same effect on the hydrolysis of esters by the action of lipase (from liver), the presence of acyl groups in the homologous series has a considerable influence on the reaction. The quantity of an ester of propionic acid which is attacked in a given time is almost exactly the mean of the quantities of the esters of acetic and butyric acids which are hydrolysed under similar conditions. The action on a formic acid ester is a little more rapid than on an acetic acid ester, but there is practically no difference in the velocity of the action on ethyl butyrate and isobutyrate. Experiments with methyl  $\beta$ -iodopropionate, ethyl acetate, and ethyl butyrate show that the introduction of the iodine atom in the  $\beta$ -position does not tend to retard the action of lipase, but rather to accelerate it. The introduction of cyanogen into an ester of acetic acid does not affect the action very considerably, the velocity being reduced at most by half; the retarding influence of the cyanoacetic acid becomes more apparent, however, when the experiment is prolonged.

E. W. W.

**Action of Radium Rays on Tyrosinase.** EDITH G. WILLCOCK (*J. Physiol.*, 1906, 34, 207—209).—Tyrosinase is an exception to the general rule that radium emanations injure ferments. It may be that the rays bring about oxidation of ordinary ferments, but that oxydase is not itself readily oxidisable, but this view is not strongly urged.

In some cases, where the ferment seemed to be strengthened by exposure to the rays, the result was at first regarded as due to a small amount of hydrogen peroxide formed in the medium. Fenton has shown that radium rays produce this substance from water; this view was not confirmed on examination, for neither glycerol nor water exposed to the rays strengthened the ferment.

W. D. H.

## Organic Chemistry.

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**Volatility in Various Groups of Compounds.** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 187—197. Compare *Abstr.*, 1904, i, 466).—*Nitrogen and Phosphorus Compounds.*—The difference between the boiling points of ammonia and hydrogen phosphide is approximately the same as that between the boiling points of hydrazine and liquid hydrogen phosphide. Similarly, the rise in boiling point due to the substitution of H by  $\text{NH}_2$  in ammonia is practically the same as that for the replacement of H by  $\text{PH}_2$  in hydrogen phosphide.

The replacement of a hydrogen atom by an alkyl group in hydrogen phosphide leads to a greater diminution of volatility than the analogous substitution in ammonia. The replacement of the last hydrogen atom in ammonia by  $\text{CH}_3$  leads to an increase in volatility, dimethylamine boiling at  $7^\circ$  and trimethylamine at  $3^\circ$ . In the case of hydrazine, the substitution of an ethyl group for a hydrogen atom leads to an increase of volatility but the effect is less than that due to the substitution of a hydrogen atom by a methyl group. In this respect, hydrazine resembles water, and the phenomenon in both cases is probably due to the fact that water and hydrazine are associated whilst alkyl derivatives are not. The two amino-groups of hydrazine are equivalent so far as the effect of substitution on volatility is concerned.

*Carbon and Silicon Compounds.*—It is pointed out that of the analogous hydrides, oxides, sulphides, and alkyl derivatives of these two elements, the silicon compounds are, as is to be expected, the less volatile, although this difference tends to disappear, or even to change its sign, in the case of the corresponding alkyloxy-compounds, thus  $\text{C}(\text{OEt})_4$  boils at  $158\text{--}159^\circ$ , whilst  $\text{Si}(\text{OEt})_4$  boils at  $165^\circ$ . Among the analogous halogen compounds of the elements, on the other hand, the carbon derivatives are usually the less volatile. This latter fact is not due to difference in degree of association, since several investigators have shown that the two tetrachlorides are associated to about the same extent.

T. A. H.

**Use of Metallic Oxides as Catalytic Oxidising Agents.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1906, 142, 1394—1395).—A claim for priority (compare Matignon and Trannoy, this vol., ii, 427). The authors have for some time been engaged on the investigation of the catalytic oxidising action of metallic oxides and find that when a mixture of methane and oxygen is passed over heated copper oxide, the latter becomes incandescent and remains so if the heating is discontinued. The hydrocarbon is almost completely burnt to carbon dioxide and water, a small quantity of formaldehyde and formic acid being formed. Similar results are obtained with pentane, hexane, and heptane, and the copper oxide can be replaced by the oxides of cobalt or nickel.

M. A. W.

**Principle of Partition ("Vertheilungsprincip").** ARTHUR MICHAEL (*Ber.*, 1906, 39, 2138—2143).—A theoretical paper, not suitable for abstraction, further elaborating the author's attempt to account for various organic reactions by considering the sum of the influences exerted by all the atoms in the molecule (*Abstr.*, 1900, i, 321).

A. McK.

**Application of the Principle of Partition. III. Action of Chlorine on Hexane.** ARTHUR MICHAEL and HAROLD J. TURNER (*Ber.*, 1906, 39, 2153—2156. Compare preceding abstract and this vol., i, 551, 559).—When chlorine is passed into boiling hexane in diffused daylight, the resulting mixture of chlorohexanes contains more than 10 per cent. of  $\alpha$ -chlorohexane; more  $\beta$ -chlorohexane than  $\gamma$ -chlorohexane is formed.

A. McK.

**Preparation of *s*-Tetrachloroethane and Hexachloroethane.** FRIEDRICH MICHEL (*Zeit. angew. Chem.*, 1906, 19, 1095—1097).—Disulphur dichloride ( $S_2Cl_2$ ) mixed with 1 per cent. by weight of reduced iron is saturated with chlorine, the excess of this gas being subsequently removed by a current of carbon dioxide. Dry acetylene is then passed into this liquid, the whole being kept at a temperature of  $40^\circ$ . As soon as the acetylene ceases to be absorbed, the excess is removed by a stream of dry carbon dioxide, and chlorine is once more bubbled through the liquid; the above cycle of changes is then repeated until there appears to be no further absorption. The liquid is finally saturated with acetylene, and is then shaken up with water to remove any chloride of sulphur and distilled with steam. The oily distillate, after washing with sodium carbonate, is fractionally distilled, when a mixture of *s*-tetrachloroethane, pentachloroethane, and hexachloroethane is obtained, the two latter only in small quantity. Hexachloroethane is obtained by alternately passing dry acetylene and dry chlorine into gently boiling disulphur dichloride mixed with from 1 to 2 per cent. of reduced iron and contained in a reflux apparatus. Finally the solution is saturated with chlorine, and, while hot, poured off from a dark, amorphous solid and allowed to cool. A portion of the hexachloroethane hereby crystallises out, and can be purified by sublimation and crystallisation from alcohol; the mother liquors are then put back again and alternately saturated with chlorine and acetylene.

P. H.

**Decomposition of Copper Sulphate by Methyl Alcohol.** VICTOR AUGER (*Compt. rend.*, 1906, 142, 1272—1274. Compare Klepl, *Abstr.*, 1882, 1274; de Bruyn, *Abstr.*, 1893, i, 244; de Forcrand, *Abstr.*, 1886, 524).—Hydrated copper sulphate is soluble to the extent of 11.5 per cent. in methyl alcohol at  $0^\circ$ , and the *basic sulphate*,  $3CuSO_4 \cdot CuO \cdot 4CH_3O$ , separates from the solution in the form of rosettes of small, green needles; this compound, which can be obtained in much larger quantity by the prolonged boiling of a 2.5 per cent. solution of copper sulphate in methyl alcohol, or by shaking anhydrous copper sulphate in contact with methyl alcohol for a week,



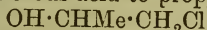
is stable in a vacuum over sulphuric acid, but decomposes slowly at  $110^{\circ}$  or in contact with moist air.

Pickering has shown (*Chem. News*, 1883, 47, 181) that when a 1.28 per cent. aqueous solution of copper sulphate is boiled, 2.5 per cent. of the copper is deposited in the form of the basic salt,  $6\text{CuO} \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ , but a methyl alcohol solution of the same dilution deposits 73 per cent. of the copper as the above basic salt.

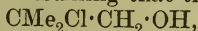
Methyl alcohol decomposes zinc sulphate, forming a basic salt, and also, but to a much less extent, cobalt or nickel sulphates. Ethyl alcohol is much less active than methyl alcohol in promoting the decomposition of copper sulphate.

M. A. W.

**Application of the Principle of Partition. IV. Addition of Hypochlorous Acid to *iso*Butylene.** ARTHUR MICHAEL and VIRGIL L. LEIGHTON (*Ber.*, 1906, 39, 2157—2163. Compare this vol., i, 550, 559).—Markownikoff first showed that the propylene chlorohydrin, formed by the addition of hypochlorous acid to propylene, has the formula



and not  $\text{CHMeCl} \cdot \text{CH}_2 \cdot \text{OH}$ . The authors now show that Butleroff and Henry are incorrect in assuming that the chlorohydrin,



is formed by the addition of hypochlorous acid to *isobutylene*; the isomeric compound,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Cl}$ , is produced. The rule is submitted that the addition of hypochlorous acid to  $\alpha$ -alkylenes leads to the formation of alkylene chlorohydrins, where the chlorine atom is attached to a terminal carbon atom which was previously unsaturated. This is not actually contradictory to the principle of distribution enunciated by one of the authors.

*isoButylene chlorohydrin* is a colourless oil which boils at  $128^{\circ}$  (corr.) and has a sp. gr. 1.0663 at  $20^{\circ}$ . At the ordinary temperature, it is very slowly decomposed by water into hydrochloric acid and *isobutaldehyde*. Its constitution was deduced from its behaviour on dehydration with phosphoric oxide when *chloroisobutylene* was formed. A. McK.

**Application of the Principle of Partition. II. Constitution of the Hexyl Alcohol prepared from Mannitol Hexylene.** ARTHUR MICHAEL and ROBERT N. HARTMAN (*Ber.*, 1906, 39, 2149—2152. Compare this vol., i, 550).—The product obtained by the addition of water to hexylene from mannitol does not consist of  $\beta$ -hexanol alone, but is a mixture of  $\beta$ -hexanol and  $\gamma$ -hexanol. The product was submitted to gentle oxidation and the constitution of the resulting ketone mixture determined by the semicarbazide method (*loc. cit.*). The conclusion is drawn that the hexanol mixture contains about 77 per cent. of  $\beta$ -hexanol and 23 per cent. of  $\gamma$ -hexanol.

A. McK.

**Acetyl Chloride as a Reagent for Pinacolyl Alcohols.** MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1906, 134—139).—Henry's experiments (this vol., i, 329) on the action of acetyl chloride on methyl*tert.*-butylcarbinol and dimethyl*isopropyl*carbinol have been repeated, and in both cases the author obtained, as a principal product, an ester boiling at



135—142°. The dimethylisopropylcarbinol used was prepared by Masson's method (Abstr., 1901, i, 249) and differed slightly in boiling point from that used by Henry.

The author has already shown that in the case of the action of hydrogen bromide on  $\psi$ -butylethylene ( $\gamma\gamma$ -dimethyl- $\Delta^{\alpha}$ -butylene) (this vol., i, 476) the course of the reaction is dependent on the purity of the hydrocarbon, and suggests that it will be necessary to repeat Henry's experiments with carefully purified specimens of the two alcohols before his method of differentiating between the *sec.*- and *tert.*-alcohols can be accepted.

T. A. H.

**Etherates of Magnesium Bromide and Iodide. II. The Monoetherate of Magnesium Bromide.** BORIS N. MENSCHUTKIN (*Zeit. anorg. Chem.*, 1906, 49, 207—212. Compare Abstr., 1904, i, 215; this vol., i, 131, 132).—The solubility relations of ether and the monoetherate of magnesium bromide have been investigated. The saturated solution of the monoetherate in ether is stable between 30° and 158°, the solubility decreasing regularly from 49.1 to 41 per cent. by weight of magnesium bromide between 0° and 158°; below 30°, addition of a trace of dietherate causes the separation of this substance in crystals, whilst above 158° a second liquid layer is formed with separation of monoetherate. When a quantity of etherate corresponding with about 4 per cent. of magnesium bromide is present, the second layer disappears and the solubility curve can be followed to higher temperatures; at 170°, the solution contains only about 0.13 per cent. of magnesium bromide. The solubility curves of ether in the saturated solution of the monoetherate and of the latter solution in ether have also been determined; the systems are stable between 22.8° and 158°.

The complete results obtained in the present and former papers (Abstr., 1904, i, 215) for the equilibrium relations of ether and the mono- and di-etherates are represented diagrammatically.

G. S.

**New Synthesis of Methyl Ethyl Xanthate.** HARRY S. FRY (*J. Amer. Chem. Soc.*, 1906, 28, 796—798).—When magnesium is allowed to react with a solution of carbon disulphide in methyl alcohol, magnesium methyl xanthate is produced. If the product of the reaction is treated with ethyl bromide and the mixture is afterwards acidified with dilute sulphuric acid, methyl ethyl xanthate,  $\text{OMe}\cdot\text{CS}\cdot\text{SEt}$ , is obtained in a yield of 62.5 per cent. of the theoretical.

E. G.

**Sulphoacetic Acid.** OTTO STILlich (*J. pr. Chem.*, 1906, [ii], 73, 538—544. Compare Abstr., 1905, i, 318).—The yield of sulphoacetic acid, obtained on heating glacial acetic acid with sulphuric acid, depends on the temperature and the amount of water present. The product is isolated as barium sulphoacetate, which, when heated with aniline sulphate in aqueous solution, forms *aniline hydrogen sulphoacetate*; this crystallises in glistening, nacreous leaflets and melts at 187—188°. Contrary to Baumstark's statement (*Annalen*, 1866, 140, 81), the formation of sulphoacetic acid by the interaction of chlorosulphonic and glacial acetic acids commences at 40°, the yield increasing

to about 30 per cent. as the temperature rises to  $140^{\circ}$ ; above  $80^{\circ}$ , carbon dioxide and sulphur dioxide are formed. The barium salt is obtained in an 83 per cent. yield by Franchimont's method (Abstr., 1881, 716) or in a 92 per cent. yield by boiling chloroacetic acid with sodium sulphite and sodium carbonate in aqueous solution and precipitating the product with barium chloride.

Free sulphoacetic acid is prepared by treating the barium salt with sulphuric acid. It is moderately stable towards concentrated sulphuric acid, commencing to evolve carbon dioxide at  $190^{\circ}$  and sulphur dioxide only at  $210^{\circ}$  (compare Carius, *Annalen*, 1862, 124, 55).

Ammonium sulphoacetate,  $C_2H_2O_5S(NH_4)_2$ , crystallises in needles, melts at  $153-173^{\circ}$ , is not hygroscopic, and has an acid reaction to litmus. The strontium salt,  $C_2H_2O_5SSr \cdot H_2O$ , formed by adding strontium chloride to the barium salt in aqueous solution, crystallises in pointed needles and loses  $H_2O$  at  $230-240^{\circ}$ . The calcium salt forms small prisms containing  $1\frac{1}{6}H_2O$  (compare Franchimont, Abstr. 1888, 1177).  
G. Y.

**Derivatives of Sebacic Acid.** FRIEDRICH KRAFFT (*Ber.*, 1906, 39, 2193—2197. Compare Phookan and Krafft, Abstr., 1892, 1180).—Decamethyleneimine hydrochloride is obtained in a 65—70 per cent. yield if the mixture of sodium chloride and decamethylenediamine formed by reduction of sebacamide is heated under 100—120 mm. pressure. The free base, boiling at  $100-102^{\circ}$  under 13 mm. pressure, reacts with benzoyl chloride in a freezing mixture, forming *benzoyl-decamethyleneimine*,  $\begin{matrix} CH_2 \cdot [CH_2]_3 \cdot CH_2 \\ CH_2 \cdot [CH_2]_3 \cdot CH_2 \end{matrix} > NBz$ . This melts at  $27.5-28^{\circ}$ , boils at  $175^{\circ}$  in a vacuum, is readily soluble in alcohol or ether, and when oxidised by aqueous potassium permanganate at  $35-40^{\circ}$  yields *benzoyl-i-aminodecoic acid*,  $NHBz \cdot [CH_2]_9 \cdot CO_2H$ , which separates from alcohol or hot water in small, white crystals and melts at  $74^{\circ}$ . The barium salt,  $(C_{17}H_{24}O_3N)_2Ba$ , is described. When heated in a vacuum, the acid decomposes, forming *i-aminodecoic anhydride*,  $C_9H_{18} \begin{matrix} CO \\ | \\ NH \end{matrix}$ , which solidifies to a white, crystalline mass, melts at  $64-66^{\circ}$ , and boils at  $200-205^{\circ}$  in a vacuum.

The *hydrochloride* of *i-aminodecoic acid* is formed by heating the benzoyl derivative with concentrated hydrochloric acid at  $110-120^{\circ}$  in a sealed tube; it forms deliquescent crystals, and when treated with silver oxide yields the free *acid*,  $NH_2 \cdot [CH_2]_9 \cdot CO_2H$ . This melts and decomposes at  $164^{\circ}$ , is readily soluble in water, but less so in alcohol, and is insoluble in ether. The *platinichloride*,  $(C_{10}H_{21}O_2N)_2 \cdot H_2PtCl_6$ , was analysed.  
G. Y.

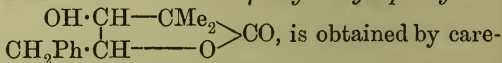
**Abnormal Dehydration of Hydroxyalkylpivalic Esters.** I. EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, iii], 35, 360—373. Compare following abstract).—*Ethyl  $\beta$ -hydroxy-3-vinylpivalate* [ *$\beta$ -hydroxy- $\alpha\alpha$ -dimethyl- $\Delta^{\gamma}$ -pentenoate*],  
 $CH_2:CH \cdot CH(OH) \cdot CMe_2 \cdot CO_2Et$ ,  
prepared by condensing ethyl bromoisobutyrate with acraldehyde, is a

viscous liquid and boils at  $106^{\circ}$  under 19 mm. pressure. The *phenylurethane* of the ester is crystalline and melts at  $66^{\circ}$ . The *free acid* obtained by hydrolysing the ethyl ester with alcoholic potash is viscous, boils at  $159^{\circ}$  under 23 mm. pressure, and on bromination yields an amorphous *dibromide*. The *calcium* and *barium* salts crystallise with 3 and 5 mols. of water respectively. The *phenylurethane* of the acid crystallises in needles from a mixture of benzene and light petroleum and melts at  $90-95^{\circ}$ .

When ethyl  $\beta$ -hydroxy- $\alpha\alpha$ -dimethyl- $\Delta\gamma$ -pentenoate is dehydrated with phosphoric oxide in presence of benzene, a mixture of gaseous and liquid hydrocarbons, tetramethylsuccinic acid, and some  $\delta$ -phenyl- $\alpha\alpha$ -dimethyl- $\Delta^{\beta}$ -pentenoic acid are produced. When the operation is conducted in presence of toluene, a mixture of *o*- and *p*-tolylidimethyl- $\Delta^{\beta}$ -pentenoic acids is formed, whilst in presence of chloroform much gas is evolved and almost complete decomposition ensues.  $\gamma$ -Benzyl- $\alpha\alpha$ -dimethylvinylacetic acid [ $\delta$ -phenyl- $\alpha\alpha$ -dimethyl- $\Delta^{\beta}$ -pentenoic acid],



best purified through its *calcium* salt, is a viscous liquid and boils at  $195^{\circ}$  under 20 mm. pressure, and on bromination yields an oily unstable *dibromide*. The *methyl* ester, best obtained by the interaction of the acid chloride with methyl alcohol, is liquid and boils at  $154^{\circ}$  under 17 mm. pressure. The *ethyl* ester, similarly prepared, boils at  $154^{\circ}$  under 12 mm. pressure. The *acid chloride* is a liquid with a disagreeable, irritating odour, and boils at  $158-159^{\circ}$  under 20 mm. pressure. The *amide* crystallises from ether in silky spangles and melts at  $104-105^{\circ}$ ; the *anilide* separates from a mixture of ether and light petroleum in long prisms and melts at  $90^{\circ}$ , and the *phenylhydrazide* is crystalline and melts at  $99^{\circ}$ .  $\beta$ -Hydroxy- $\delta$ -phenyl- $\alpha\alpha$ -dimethyl- $\gamma$ -valerolactone,



is obtained by careful oxidation of  $\delta$ -phenyl- $\alpha\alpha$ -dimethyl- $\Delta^{\beta}$ -pentenoic acid with potassium permanganate. It crystallises from a mixture of benzene and light petroleum and melts at  $100^{\circ}$ . The final oxidation products of  $\delta$ -phenyl- $\alpha\alpha$ -dimethyl- $\Delta^{\beta}$ -pentenoic acid are dimethylmalonic and benzoic acids, the latter being probably formed from phenylacetic acid.

The  $\delta$ -tolyl- $\alpha\alpha$ -dimethyl- $\Delta^{\beta}$ -pentenoic acid, obtained on dehydrating ethyl hydroxydimethylpentenoate in presence of toluene, is a viscous liquid and boils at  $199^{\circ}$  under 16 mm. pressure, and must consist of a mixture of the ortho- and para-derivatives, since on oxidation with permanganate it yields a mixture of terephthalic and *p*- and *o*-toluic acids. The other oxidation products are *o*- and *p*-tolualdehyde, identified by their *semicarbazones*, which melt respectively at  $212^{\circ}$  and  $234^{\circ}$ , and dimethylmalonic acid. It is pointed out that *p*-toluic acid is not, as is generally stated, readily soluble in warm water or steam.

T. A. H.

Dehydration of  $\beta$ -Hydroxy- $\beta$ -alkylpivalic Esters. Parts III and IV. ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 298-305, 355-360. Compare this vol., i, 230, 396).—Ethyl  $\beta$ -hydroxy- $\beta\beta$ -dimethylpivalate [ $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyrate],



$\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , prepared by condensing acetone with ethyl bromoisobutyrate, boils at  $91^\circ$  under 17 mm. pressure (compare Reformatsky and Plesconosoff, Abstr., 1896, i, 128). The *acetyl* derivative is a viscous liquid and boils at  $119^\circ$  under 23 mm. pressure. When dehydrated with phosphoric oxide in the usual way (*loc. cit.*), the ester yields *ethyl  $\alpha\alpha$ -dimethylisopropenylacetate* [ $\alpha\alpha\beta$ -trimethyl- $\Delta\beta$ -butenoate],  $\text{CH}_2\text{:CMe}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ . This is a mobile liquid of pleasant odour and boils at  $161^\circ$ . The *methyl* ester is similar and boils at  $148^\circ$ . The *free acid*, obtained with difficulty by hydrolysing the ethyl ester with alcoholic potash, is crystalline, melts at  $35^\circ$ , boils at  $117^\circ$  under 28 mm. pressure, and is very hygroscopic. The hydrated *calcium*, *barium*, and *lead* salts are crystalline. The *chloride* is a mobile liquid with a sharp disagreeable odour and boils at  $60^\circ$  under 30 mm. pressure. The *amide* crystallises from ether in pearly lamellæ and melts at  $107$ – $108^\circ$ , the *anilide* forms needles from a mixture of ether and light petroleum and melts at  $61^\circ$ ; the *phenylhydrazide* crystallises from boiling alcohol and melts at  $141^\circ$ ; and the  $\beta$ -*naphthylamide* separates from boiling alcohol in small needles and melts at  $94^\circ$ .

$\beta\gamma$ -Dibromo- $\alpha\alpha\beta$ -trimethylbutyric acid,  $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , prepared by brominating  $\alpha\alpha\beta$ -trimethylbutenoic acid in carbon disulphide at  $0^\circ$ , crystallises from a mixture of ether and light petroleum and melts at  $125$ – $126^\circ$ . The *methyl* ester is liquid and boils at  $130^\circ$  under 10 mm. pressure.

On reduction with sodium, ethyl trimethylbutenoate yields the corresponding  $\beta\beta\gamma$ -trimethyl- $\Delta\gamma$ -butenol,  $\text{CH}_2\text{:CMe}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ . This is a mobile liquid of slight odour and boils at  $152^\circ$ . The *acetate* has a pleasant odour and boils at  $170$ – $171^\circ$ , and the *phenylurethane* forms splendid needles from light petroleum and melts at  $73^\circ$ .

When oxidised with permanganate, trimethylbutenoic acid furnishes methyl isopropyl ketone, trimethylmalic acid, which melts and decomposes at  $200$ – $210^\circ$  (compare Auwers and Campenhausen, Abstr., 1896, i, 424, and Komppa, *ibid.*, i, 597), and  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyrolactone,  $\text{OH}\cdot\text{CMe}\cdot\text{CMe}_2\cdot\text{CH}_2\text{---O}>\text{CO}$ , which crystallises from dry ether and melts at  $103^\circ$ .

*Ethyl  $\beta$ -hydroxy- $\beta$ -phenyl- $\beta$ -methylpivalate* [ $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha\alpha$ -dimethylbutyrate], prepared by condensing acetophenone with ethyl bromoisobutyrate, is a syrupy liquid, boils at  $154^\circ$  under 10 mm. pressure, and on treatment with dilute alcoholic potash yields acetophenone and isobutyric acid. Some dyponone is produced as a by-product in the primary condensation: *dyponone semicarbazone* crystallises from benzene and melts at  $151^\circ$ . When ethyl  $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha\alpha$ -dimethylbutyrate is dehydrated with phosphoric oxide it yields *ethyl phenyldimethylvinylacetate* [ $\beta$ -phenyl- $\alpha\alpha$ -dimethyl- $\Delta\beta$ -butenoate],  $\text{CH}_2\text{:CPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ . This is a liquid and boils at  $132^\circ$  under 10 mm. pressure. The *methyl* ester boils at  $133^\circ$  under 19 mm. pressure. The *free acid* is a syrup and boils at  $167^\circ$  under 8 mm. pressure. The *potassium*, *calcium*, and *lead* salts are crystalline. The *chloride* is a mobile liquid of disagreeable odour and boils at  $130^\circ$  under 13 mm. pressure. The *amide* crystallises from ether and melts at  $118^\circ$ , the *anilide* separates from alcohol in needles and melts at



85°, and the *phenylhydrazide* forms lamellæ from alcohol and melts at 159°.

On bromination in carbon disulphide at 0°, phenyldimethylbutenoic acid yields *βγ-dibromo-β-phenyl-α-dimethylbutyric acid*,



which crystallises from benzene and melts and decomposes at 165°.

When phenyldimethylbutenoyl chloride is treated with zinc methyl, *β-phenyl-α-dimethyl-β-allyl methyl ketone*,  $\text{CH}_2\text{:CPh} \cdot \text{CMe}_2 \cdot \text{COMe}$ , is produced. It is a pleasant-smelling liquid, which boils at 123° under 10 mm. pressure. The *semicarbazone* crystallises from alcohol and melts at 192°.

*γ-Phenyl-ββ-dimethyl-Δ<sup>4</sup>-butenol*,  $\text{CH}_2\text{:CPh} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , obtained by reducing ethyl phenyldimethylbutenoate with sodium, is a sweet-smelling, syrupy liquid, which boils at 141° under 17 mm. pressure and is not volatile in steam. The *acetate* boils at 145° under 15 mm. pressure.

T. A. H.

**Xanthophanic and Glaucophanic Acids.** CARL LIEBERMANN (*Ber.*, 1906, 39, 2071—2088).—Claisen's xanthophanic and glaucophanic acids (*Abstr.*, 1897, i, 594) are shown by Zeisel's method to contain respectively two and approximately three ethoxyl groups, and should therefore, the author considers, be called ethyl xanthophanic and ethylglaucophanic acids [xanthophanic acid ethyl ether and glaucophanic acid ethyl ether]. From the chloroform or benzene mother liquor of the crude xanthophanic acid ethyl ether (*loc. cit.*), a *substance*,  $\text{C}_{20}\text{H}_{22}\text{O}_5$ , is obtained, which crystallises rapidly from alcohol or light petroleum in colourless, glassy needles, contains two ethoxyl groups, melts at 97°, and is very similar to Claisen's ethyl methenylbisacetoacetate, but differs from it by its insolubility in alkalis; the *bromophenylhydrazone*,  $\text{C}_{26}\text{H}_{27}\text{O}_4\text{N}_2\text{Br}$ , crystallises in yellow needles and melts at 178°. After the estimation of ethoxyl in this by-product, the de-alkylated residue is obtained from alcohol in colourless needles which melt at 265° and, after sublimation, at 280°; it has an acid reaction and does not give a coloration with ferric chloride.

Xanthophanic acid and glaucophanic acid methyl ethers are obtained in better yield than the corresponding ethyl compounds when methyl methoxymethyleneacetoacetate (2 mols.) and methylsodioacetoacetate (1 mol.) are melted together on the water-bath. The *xanthophanic acid methyl ether*,  $\text{C}_{16}\text{H}_{16}\text{O}_8$ , is separated from the accompanying sodium glaucophanate methyl ether by solution in chloroform. It separates from benzene in red needles and melts at 179°; from the mother liquor, dark blue metallic prisms are obtained, having the same composition and melting point. *Sodium glaucophanate methyl ether*,  $\text{C}_{24}\text{H}_{19}\text{O}_{12}\text{Na}$ , forms greenish-blue crystals insoluble in chloroform. The *acid*,  $\text{C}_{24}\text{H}_{20}\text{O}_{12}$ , melts and decomposes at 206°. The by-product in the reaction is a *substance*,  $\text{C}_{18}\text{H}_{18}\text{O}_5$ , which separates from light petroleum in colourless needles, melts at 133°, is insoluble in alkalis, and contains methoxyl; the de-methylated residue is a colourless acid, melts at 260°, and sublimes in colourless needles.

Sodium methoxide and xanthophanic acid ethyl ether react in benzene solution to form a *substance* which separates from benzene

in colourless crystals, melts at  $143^{\circ}$ , dissolves in alkalis, and gives a red coloration with ferric chloride. Xanthophanic acid methyl ether and glaucophanic acid ethyl and methyl ethers form analogous compounds.

Magnesium methoxide reacts with xanthophanic acid ethyl ether to form a *substance* which crystallises in yellow needles and melts at  $160\text{--}161^{\circ}$ . With glaucophanic acid ethyl ether, magnesium methoxide reacts to form two substances: the one is sparingly soluble in benzene and acetic acid and melts at  $213^{\circ}$ , the other dissolves readily and melts at  $199^{\circ}$ ; both crystallise in yellow needles and are soluble in a cold solution of sodium carbonate.

Magnesium methoxide and xanthophanic acid methyl ether form a *substance* which crystallises in yellow needles, melts and decomposes at  $162^{\circ}$ , and forms a *bromophenylhydrazone* melting at  $224^{\circ}$ . The substance obtained by the action of magnesium methoxide on xanthophanic acid methyl or ethyl ether or on glaucophanic acid ethyl ether is decomposed by a concentrated solution of potassium hydroxide, forming an *acid* which crystallises in white needles, melts and decomposes at  $255^{\circ}$ , gives a red coloration with ferric chloride, and yields resacetophenone on sublimation; the same acid can be directly obtained from xanthophanic acid ethyl or methyl ether.

Xanthophanic acid ethyl ether reacts with semicarbazide hydrochloride in the presence of methyl alcohol and sodium acetate to form *hydrazodicarbonamide*,  $(\text{NH}_2 \cdot \text{CO} \cdot \text{NH})_2$ , which crystallises in colourless needles and melts at  $253^{\circ}$ , and a *substance*,  $\text{C}_{19}\text{H}_{23}\text{O}_8\text{N}_3$ , which melts at  $194^{\circ}$ , does not regenerate xanthophanic acid by treatment with hydrochloric acid, and does not show the following characteristic test for the acid. When xanthophanic acid methyl or ethyl ether is warmed with concentrated sulphuric acid, the red colour of the solution suddenly disappears and a yellow, fluorescent solution is obtained, from which can be isolated a *substance*,  $\text{C}_{14}\text{H}_{10}\text{O}_7$ , which crystallises in golden scales, melts and decomposes at  $185^{\circ}$ , dissolves in alkali without fluorescence, and forms a brominated derivative melting and decomposing at  $270\text{--}275^{\circ}$ .

When sodium glaucophanate ethyl or methyl ether is warmed with dilute nitric acid, a *substance* is obtained which does not contain nitrogen, crystallises in yellow needles, becomes brown at  $170^{\circ}$ , melts at  $194^{\circ}$ , and contains ethoxyl.

C. S.

**Decomposition of the Oxalates of the Alkaline Earths by Aqueous Solutions of Alkali Sulphates.** H. CANTONI (*Arch. Sci. phys. nat.*, 1906, [iv], 21, 469—494).—Solutions of alkali sulphates were added to the oxalates of the alkaline earths, and the quantity of the oxalate which passed into solution estimated by permanganate. Complete tables of the results are given. In general, potassium sulphate has a greater effect than the sulphates of sodium or ammonium, and the decomposition of the oxalate is greatest for the barium salt and least for the calcium salt. This is what would be expected from the relative solubilities. Thus, in the case of a  $4/25N$  solution of potassium sulphate after nine hours, the decomposition by the oxalate of barium reached 50 per cent., by oxalate of strontium 6.88 per cent., and by calcium oxalate 0 per cent.

L. M. J.

**Preparation of Adipic Acid.** ERIK ROSENLEW (*Ber.*, 1906, 39, 2202. Compare Mannich, this vol., i, 432).—The conditions are detailed under which adipic acid is obtained in a 70—75 per cent. yield, by the oxidation of *cyclohexanone* by means of potassium permanganate in sodium carbonate solution. G. Y.

**Antimony Tartrate and its Ethyl Ester.** J. BOUGAULT (*J. Pharm. Chim.*, 1906, [vi], 23, 465—469).—Antimonious oxide is dissolved in an aqueous solution of tartaric acid, and the liquid allowed to evaporate spontaneously to a syrup. On the addition of acetone, a precipitate is formed which rapidly becomes crystalline, and consists of the tartrate,  $\text{SbC}_4\text{H}_3\text{O}_6$  (this vol., i, 336), containing 1 mol. of acetone, which it loses at  $100^\circ$ . When the anhydrous tartrate is dissolved in a solution of tartaric acid in alcohol, an *ethyl* ester,  $\text{SbC}_4\text{H}_2\text{O}_6\text{Et}$ , slowly separates in small, slender needles. This is dissociated by water with the partial precipitation of antimonious oxide. When dissolved in a solution of potassium hydrogen carbonate, some antimonious oxide is precipitated, but this redissolves on boiling, forming tartar emetic. An aqueous solution of potassium tartrate dissolves the ester, giving potassium ethyl tartrate and tartar emetic. T. A. H.

**Methylene Compounds.** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 206—226).—The first portion of this memoir is devoted to the discussion of De Sonay's work (*ibid.*, 1893, 26, 629, and 1894, 28, 102) on the chlorination of methyl ether and methylal in the light of the new results obtained by Descudé (see following abstract), and it is pointed out that De Sonay's dichloromethylal probably had the formula  $\text{CCl}_2(\text{OMe})_2$  in place of  $\text{CH}_2(\text{O}\cdot\text{CH}_2\text{Cl})_2$  as he supposed. This correction of De Sonay's work indicates that the chlorination of methylal proceeds normally, the hydrogen atom of the methylene group being replaced before those of the methyl groups.

In the second portion of the memoir, a number of analogies between derivatives of "oxymethylene" and the oxides of the heavy metals are pointed out and illustrated by examples, thus: the compound  $(\text{CH}_2)_3\text{O}_2\text{Cl}_2$  is regarded as similar in constitution to the mineral mendipite,  $\text{Pb}_3\text{O}_2\text{Cl}$ .

In the third section, it is pointed out that ethylidene compounds (methyl derivatives of methylene) may be regarded as forming a series parallel to that of the methylene compounds.

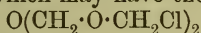
In connection with the order of replacement of hydrogen atoms by chlorine in substances of these types, it is noted that the action of hydrogen chloride on a mixture of acetaldehyde and alcohol gives rise first to the compound  $\text{CHMeCl}\cdot\text{OEt}$ , and eventually to  $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{OEt}$ , a reaction which appears to be analogous to the production of  $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CH}_2\text{Cl}$  from  $\text{CH}_2\text{Cl}\cdot\text{OMe}$ , the chlorine in both cases replacing a hydrogen atom in an unattacked methyl group in preference to entering a group in which substitution has already occurred (compare Littirschaid, *Abstr.*, 1904, i, 364). T. A. H.

**Order of Substitution of Hydrogen by Chlorine in Methylal.** MARCEL DESCUDÉ (*Bull. Acad. roy. Belg.*, 1906, 198—205).—In addition to the dichloromethyl oxide (*Abstr.*, 1904, i, 546), pro-



duced when trioxymethylene is treated with phosphorus trichloride in the presence of zinc chloride, there is formed some *dichloromethylal*,  $\text{CH}_2(\text{O}\cdot\text{CH}_2\text{Cl})_2$ . This boils at  $65-67^\circ$  under 15 mm. pressure, and with slight decomposition at  $166^\circ$  under atmospheric pressure. It has sp. gr. 1.352 at  $11^\circ/11^\circ$ , and is decomposed immediately by water, yielding hydrogen chloride and formaldehyde, and by alcohols forming water, hydrogen chloride, and monochloromethyl oxide.

When dichloromethyl oxide is heated with trioxymethylene in a closed tube, some dichloromethylal is formed, but the principal reaction is more complex, a *product* which may have the formula



being formed. This is liquid and boils at  $100-102^\circ$  under 15 mm. pressure.

The author points out that the several chlorine derivatives of methylal described by De Sonay (*Bull. Acad. roy. Belg.*, 1893, 26, 647) probably exist, but the boiling points ascribed to them by this author indicate that the constitutions he assigned to them are probably erroneous.

T. A. H.

**Depression of the Temperature of Reaction in Syntheses with Organic Chloro-compounds.** ALFRED WOHL (*Ber.*, 1906, 39, 1951—1954. Compare Hesse, this vol., i, 375).—The action of  $\beta$ -chloropropaldehyde diethylacetal on potassium cyanide (Wohl, Schäfer, and Thiele, this vol., i, 105) and on ethyl sodiocyanoacetate, of alcoholic ammonia on chloroacetaldehyde diethylacetal and on *p*-chloro- and *o*-chloro-nitrobenzenes, of ethyl chloride on potassium phenoxide, of benzotrichloride on sodium amyloxide, and of *as*-dichloroacetone on sodium acetate take place at lower temperatures and with increased yields if  $1/10-1/5$  mol. of potassium iodide is added for each atom of chlorine entering into the reaction. The corresponding organic iodo-compound is formed as an intermediate product, the alkali iodide being regenerated in the second stage of the reaction.

Reactions which take place readily, such as that of sodium methoxide on *p*- and on *o*-chloronitrobenzene, are not affected by addition of an alkali iodide.

G. Y.

**Application of the Principle of Partition. I. Course of the Addition of Water to  $\beta$ -Hexinene.** ARTHUR MICHAEL (*Ber.*, 1906, 39, 2143—2148. Compare this vol., i, 550).—The application of the principle of partition enunciated by the author is discussed in the case of the formation of a hexanone by the action of sulphuric acid on  $\Delta^{\beta}$ -hexinene.

$\gamma$ -Hexanone, prepared by the action of an ethereal solution of zinc ethyl on propionyl chloride, boils at  $123-123.5^\circ$  under 765 mm. pressure.

Attempts to separate  $\beta$ -hexanone from  $\gamma$ -hexanone by means of sodium hydrogen sulphite are described. In a mixture of  $\beta$ -hexanone and  $\gamma$ -hexanone, the amount of each may be estimated, since the former forms a semicarbazone with hydrogen semicarbazide phosphate and the latter does not.

The ketone mixture, formed by the action of sulphuric acid on



$\Delta^{\beta}$ -hexinene, was fractionated, and the ratio of  $\beta$ -hexanone to  $\gamma$ -hexanone in each individual fraction was estimated by means of the semicarbazide method described.

A. McK.

**Melezitose and Turanose.** GEORGES TANRET (*Compt. rend.*, 1906, 142, 1424—1426. Compare Berthelot, *Abstr.*, 1877, i, 451; Villiers, *ibid.*; Alechin, *Abstr.*, 1886, 683; 1890, 733; Markownikoff, *Abstr.*, 1885, 943).—Melezitose is hydrolysed by heating with 20 per cent. acetic acid solution, yielding turanose and dextrose; after destroying the dextrose by means of yeast, the turanose can be isolated from an alcoholic extract of the residue in the form of transparent, non-crystalline, rounded grains which contain alcohol, have the composition  $C_{12}H_{22}O_{11} \cdot \frac{1}{2}C_2H_6O$ , melt at 60—65°, and lose their alcohol at 100°, yielding the pure sugar, which has  $[\alpha]_D + 71.8^\circ$ , does not exhibit mutarotation, and has a reducing power of 60, that of dextrose being taken as 100.

Turanose is not attacked by the ordinary soluble ferments, such as emulsin or diastase, but is readily hydrolysed by mineral acids, yielding an equal molecular mixture of dextrose and lævulose, and not dextrose only as stated by Alechin (*Abstr.*, 1890, 733).

M. A. W.

**Behaviour of Starch on Hydrolysis with Moderately Concentrated Sulphuric Acid.** BERNHARD TOLLENS (*Ber.*, 1906, 39, 2190—2193).—The product of the hydrolysis of potato starch with 8 per cent. sulphuric acid contains dextrose, at most only traces of mannose, and no galactose. The author concludes that the mannose and galactose obtained on hydrolysis of reindeer mosses (Ulander and Tollens, this vol., ii, 193) were derived from the hemicelluloses of the lichens and not from glucoses.

G. Y.

**Cellulose Acetates.** HERMANN OST (*Zeit. angew. Chem.*, 1906, 19, 993—1000).—The author is of opinion that all the acetates of cellulose described by previous authors are in reality triacetates of substances derived from the hydrolysis of ordinary cellulose.

P. H.

**Copper Alkali Cellulose.** WILHELM NORMANN (*Chem. Zeit.*, 1906, 30, 584—585).—When cotton wool is treated with a solution of copper hydroxide in sodium hydroxide, it swells up and is converted into a stable copper alkali cellulose, which on analysis is found to contain cellulose and copper oxide in the ratio  $C_{12}H_{20}O_{10} : CuO$ . The same substance may also be obtained in the form of clear, glassy threads by allowing a fine stream of copper ammonia cellulose to flow into a solution of an alkali hydroxide.

P. H.

**New Syntheses of Amines by means of Finely-divided Nickel.** ALPHONSE MAILHE (*Chem. Zeit.*, 1906, 30, 458—459. Compare *Abstr.*, 1905, i, 401, 501).—Nitriles, when reduced by hydrogen in the presence of finely-divided nickel or copper, yield a mixture of primary, secondary, and tertiary amines and ammonia, the reaction probably taking place as follows: (i)  $RCN + 2H_2 = RCH_2 \cdot NH_2$ ;

(ii)  $2\text{RCH}_2\cdot\text{NH}_2 = \text{NH}(\text{CH}_2\text{R})_2 + \text{NH}_3$ ; and (iii)  $3\text{RCH}_2\cdot\text{NH}_2 = \text{N}(\text{CH}_2\text{R})_3 + 2\text{NH}_3$ . In the case of benzonitrile, the corresponding amines are only formed with copper, nickel giving toluene. Aldoximes or ketoximes similarly give rise to a mixture of primary, secondary, and tertiary amines, but only a very small amount of the latter; the method is a very convenient one for preparing secondary amines of the type  $\text{NH}(\text{CR}^1\text{R}^2)_2$ . Acid amides, except formamide, likewise yield primary and secondary amines. When nickel is employed as the catalyst, the temperature must not be allowed to exceed  $220^\circ$ , but with copper the temperature may be anywhere between  $200^\circ$  and  $300^\circ$ .  
P. H.

**Resolution of  $\alpha$ -Aminoisovaleric Acid into its Optically Active Components.** EMIL FISCHER, KOICHI MATSUBARA, and SIEGFRIED HILPERT (*Ber.*, 1906, 39, 2320—2328).—The names "valin" and "valyl" are proposed for  $\alpha$ -aminoisovaleric acid and the group  $\text{CHMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}$  respectively.

*Formyl-i-valin*,  $\text{C}_6\text{H}_{11}\text{O}_3\text{N}$ , obtained from *i*-valin like formyl-leucine (this vol., i, 72), separates from hot water in large, rhombic plates, has an acid taste, is easily soluble in alkalis and ammonia, sinters at  $137^\circ$ , and melts at  $140$ — $145^\circ$  (corr.). After treating the hot methyl alcoholic solution with brucine, the salt of *formyl-l-valin* separates from the cold liquid in small needles, while the brucine salt of *formyl-d-valin* is obtained by evaporating the alcoholic mother liquor. The formyl derivatives, liberated by a slight excess of normal sodium hydroxide, separate from hot water in small prisms, sinter at  $150^\circ$ , and melt at  $156^\circ$  (corr.); formyl-*l*-valin has  $[\alpha]_D$  at  $20^\circ$ ,  $-13^\circ$  in alcoholic and  $16.9^\circ$  in aqueous solution, and formyl-*d*-valin has  $[\alpha]_D$   $13.05^\circ$  at  $20^\circ$  in alcoholic solution.

By hydrolysis with 10 per cent. hydrobromic acid, *d*-valin and *l*-valin are obtained in colourless, microscopic, six-sided leaflets. The former melts in a sealed tube at  $315^\circ$  (corr.), sublimes with partial anhydride formation when strongly heated, has a somewhat sweet and bitter taste, and at  $20^\circ$  in 20 per cent. hydrochloric acid has  $[\alpha]_D$   $28.75^\circ$ , and in water  $6.42^\circ$ . *l*-Valin has a sweeter taste than its isomeride, and in 20 per cent. hydrochloric acid has  $[\alpha]_D$   $-28.72^\circ$  at  $20^\circ$ .

*d*-Valinphenylcarbimide (compare Schulze and Winterstein, Abstr., 1902, i, 595) softens at  $140^\circ$ , melts and partially decomposes at  $147^\circ$  (corr.), and by rapid boiling with 20 per cent. hydrochloric acid yields *l*-phenylisopropylhydantoin, which melts at  $131$ — $133^\circ$  (corr.) ( $124^\circ$ , Schulze and Winterstein, *loc. cit.*), and has  $[\alpha]_D$   $-97.5^\circ$  at  $20^\circ$  in alcoholic solution.

*l*-Valinphenylcarbimide has  $[\alpha]_D$   $-19.02^\circ$  at  $20^\circ$ .

*l*-Phenylisopropylhydantoin melts at  $131$ — $133^\circ$  (corr.) and has  $[\alpha]_D$   $97.22^\circ$  at  $20^\circ$  in alcoholic solution.  
C. S.

**Salts of Heavy Metals with Feeble Acids and attempts to prepare Colloidal Metallic Oxides.** HEINRICH LEY and FRITZ VERNER (*Ber.*, 1906, 39, 2177—2180. Compare Ley, Abstr., 1905, i, 524; Paal and Leuze, this vol., ii, 356, 358).—Coppersuccinimide

is readily prepared by the addition of sodium hydroxide, drop by drop, to a warm aqueous solution of copper acetate and succinimide. *Cobaltsuccinimide*,  $(C_4H_4O_2N)_2Co, 6H_2O$ , formed in the same way from cobalt acetate, is obtained as a salmon-coloured, crystalline precipitate, dissolves in alcohol forming a violet solution, and is hydrolysed on addition of water. *Nickelsuccinimide*,  $(C_4H_4O_2N)_2Ni, 8H_2O$ , prepared from nickel acetate, forms light blue crystals, melts at  $110-111^\circ$ , and is more stable than the preceding salts towards water, forming a green, very dilute aqueous solution at about  $30^\circ$ ; when heated this becomes suddenly blue and opalescent, in which state it is stable in absence of air, the nickel hydroxide is thrown down by addition of salts, and the succinimide can be removed partially by hydrolysis.

Camphorimide, like succinimide, is a feeble acid. The *copper sodium* salt,  $(C_{10}H_{14}O_2N)_2Cu, 2C_{10}H_{14}O_2NNa, 10H_2O$ , is formed by the action of copper acetate on the sodium derivative in concentrated aqueous solution; it forms reddish-violet leaflets and yields blue copper hydroxide when treated with cold water, or a brown hydrated oxide when heated with water. The copper sodium salt is decomposed by acetic acid, camphorimide being formed. G. Y.

**Decomposition of Hydroxylamine in Presence of Hydrogen Ferrocyanide: Formation of Crystalline Ferrocyanide-violet and Nitroprusside.** KARL A. HOFMANN and H. ARNOLDI (*Ber.*, 1906, 39, 2204—2208. Compare Hofmann, *Abstr.*, 1905, i, 512; Tanatar, *Abstr.*, 1902, ii, 386).—When boiled with an equal weight of potassium ferrocyanide in aqueous solution, hydroxylamine hydrochloride yields ammonium chloride, potassium nitroprusside, hydrogen cyanide, nitrogen, and *ferric ammonium ferrocyanide*,  $Fe'''[(FeC_6N_6)NH_4]_2$ , which separates as a deep blue, crystalline powder with purple lustre. It is formed also when hydroxylamine hydrochloride is boiled with potassium ferricyanide in aqueous solution. In its properties, it resembles Williamson's violet. It remains unchanged when treated with water, dilute mineral acids, aqueous oxalic acid, glacial acetic acid, sodium potassium tartrate, or ferric chloride solution, or when boiled with 5 per cent. aqueous potassium hydroxide. The colour remains unchanged when the crystalline violet is digested with hydrogen sulphide solution. Ferric hydroxide is formed only slowly when the salt is digested with 4 per cent. ammonia at the ordinary temperature.

The quantitative examination of the reaction between hydroxylamine and potassium ferrocyanide shows that one-half of the latter forms the nitroprusside, whilst the other is converted into the ferric ammonium ferrocyanide. The hydrogen cyanide formed, which corresponds with one-quarter of the total ferrocyanide, does not enter into reaction with the hydroxylamine, whilst sodium nitroprusside and hydroxylamine hydrochloride form a dull blue powder only on prolonged boiling in aqueous solution. G. Y.

**Reduction of Blue Iron-cyanogen Compounds.** MORITZ KOHN (*Zeit. anorg. Chem.*, 1906, 49, 443—444).—Prussian blue and Turnbull's blue can be conveniently and rapidly reduced by the action of a concentrated sodium hydrogen sulphite solution containing a little



stannous chloride. The author considers that the reducing action is due to hyposulphurous acid produced by the action of stannous chloride. The statement in the literature, that sulphurous acid is reduced to hydrogen sulphide by stannous chloride, is only true if the latter reagent is present in excess.

G. S.

**Silicones.** OCTAVE BOUDOUARD (*Compt. rend.*, 1906, 142, 1528—1530).—The grey, amorphous residues, obtained by treating silicon steels containing 0.9 to 5.1 per cent. of silicon with hydrochloric acid until the iron is completely dissolved, have been analysed by Friedel and Ladenburg's method and also by the combustion method. The analytical data indicate that the silicones present in the residues, which evolve hydrogen when treated with alkali hydroxides, are mixtures, in variable proportions, of silicoformic anhydride and silico-oxalic acid. The residue obtained from an iron silicide, prepared by the thermite process and containing 10 per cent. of silicon, gave similar analytical numbers.

H. M. D.

**Ethyl Mercuri-*aci*-nitroacetate Anhydride.** ROLAND SCHOLL and B. NYBERG (*Ber.*, 1906, 39, 1956—1959. Compare Scholl and Schöfer, *Abstr.*, 1901, i, 359; Hantzsch and Auld, this vol., i, 471).—*Ethyl mercuri-aci-nitroacetate anhydride*,  $O \begin{smallmatrix} \text{NO} \\ \diagup \quad \diagdown \\ \text{Hg} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$ , is formed as a white, crystalline precipitate when mercuric chloride is added to a concentrated aqueous solution of ethyl ammonium *aci*-nitroacetate; it sublimes when carefully heated, detonates when strongly heated, and on ignition burns rapidly with a luminous flame. It is almost insoluble in boiling water, but dissolves readily in dilute sodium hydroxide, ammonia, or hydrochloric acid, and is not changed by potassium iodide solution. Mercuric sulphide is precipitated by hydrogen sulphide from the ammoniacal solution, whilst the hydrochloric acid solution yields mercurous chloride when boiled with phosphorous acid. The action of bromine in potassium bromide solution on the aqueous suspension leads to the formation of *ethyl dibromonitroacetate*,  $\text{NO}_2 \cdot \text{CBr}_2 \cdot \text{CO}_2\text{Et}$ , which is obtained as a colourless liquid boiling at  $105^\circ$  under 11 mm. pressure.

Mercurinitroethyl chloride (Meyer, this Journal, 1874, 27, 365, 677) has the constitution  $\text{NO}_2 \cdot \text{CHMe} \cdot \text{HgCl}$ , as it dissolves in dilute sodium hydroxide, and when treated with aqueous potassium iodide yields the yellow *iodide*,  $\text{NO}_2 \cdot \text{CHMe} \cdot \text{HgI}$ , which is soluble in an excess of potassium iodide.

*see entry, V. 902, p. 1266* G. Y.

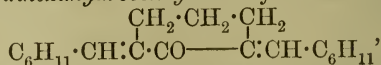
**Terpenes and Ethereal Oils. LXXXI. The Simplest ~~Men-~~ <sup>methylene</sup> Hydrocarbons of Various Ring Systems and their Conversion into Alicyclic Aldehydes.** OTTO WALLACH (*Annalen*, 1906, 347, 316—346. Compare this vol., i, 175, 194, 370).—*cyclo-Penteneacetic acid* (Wallach and Speranski, *Abstr.*, 1902, i, 800) is now found to melt at  $51-52^\circ$ ; when slowly distilled it decomposes, forming *methylenecyclopentane*,  $\begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C} : \text{CH}_2$ , which has a pene-

trating odour of leeks, boils at 78—81°, and has a sp. gr. 0.78 and  $n_D$  1.4355 at 19°. On oxidation with 1 per cent. potassium permanganate solution at 0°, it forms the *glycol*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , together with pentanone. The *glycol* melts at 39—41°, is readily soluble in all solvents, and when boiled with dilute sulphuric acid loses water, forming *cyclopentanealdehyde*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot \text{COH}$ . This is obtained as an oil which has an odour like valeraldehyde, distils in a current of steam, and forms a *semicarbazone*,  $\text{C}_7\text{H}_{13}\text{ON}_3$ , crystallising in leaflets and melting at 123—124°. The *nitrosochloride* of methylenecyclopentane,  $(\text{C}_5\text{H}_9\text{ONCl})_2$ , decomposes at 80—81°, and reacts with piperidine in alcoholic solution, forming the *nitrolamine*,  $\text{C}_6\text{H}_{10}(\text{NO}) \cdot \text{C}_5\text{H}_{10}\text{N}$ , which crystallises from alcohol and melts at 116—117°. The action of sodium methoxide on the nitrosochloride leads to the formation of a viscid, unsaturated *oxime*,  $\text{C}_6\text{H}_8\text{:NOH}$ , which, on hydrolysis with dilute sulphuric acid, yields *cyclopentenealdehyde* (v. Baeyer and v. Liebig, Abstr., 1898, i, 638).

[With EDUARD ISAAC.]—Ethyl *cyclohexanolacetate* is prepared best by the action of ethyl bromoacetate on *cyclohexanone* in benzene solution in presence of zinc. The *acid*,  $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , crystallises from a mixture of benzene and light petroleum and melts at 62—64°.

Methylenecyclohexane (Einhorn and Brandtl, Abstr., 1898, i, 407, 433; Sabatier and Mailhe, Abstr., 1904, i, 666, 809), formed by heating *cyclohexeneacetic acid*, boils at 105—106°, has a sp. gr. 0.8025 and  $n_D$  1.4501, and closely resembles  $\Delta^1$ -methylcyclohexene (Abstr., 1902, i, 750, 806). When oxidised with potassium permanganate, it forms the *glycol*,  $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , and *cyclohexanone*.

The *glycol* forms large crystals, is stable towards air in the absence of acid vapours, and melts at 76—77°. Hexahydrobenzaldehyde (Bouveault, Abstr., 1904, i, 61; Sabatier and Mailhe, *loc. cit.*) is formed by heating the *glycol* with dilute acids. It is obtained as an oil which is soluble in water, polymerises readily, boils at 161—163° under the ordinary pressure, and has a sp. gr. 0.9263 and  $n_D$  1.4495 at 19°. The *semicarbazone* melts at 167—168° (176°; Bouveault, *loc. cit.*). The aldehyde condenses with *cyclohexanone* in alcoholic sodium hydroxide solution, forming *dihexahydrobenzylidenecyclohexanone*,



which crystallises in slender needles and melts at 89—90°. With phenylhydrazine, the aldehyde condenses, developing heat and forming a *substance* which crystallises in transparent, red prisms and decomposes on exposure to air. The action of ammonia on the aldehyde in ethereal solution leads to the formation of a *product*,  $\text{C}_7\text{H}_{13}\text{N}$ , which crystallises in transparent prisms and decomposes at 104—105°.

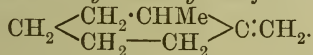
The *polymeride* of hexahydrobenzaldehyde,  $(\text{C}_7\text{H}_{12}\text{O})_2$ , is obtained as a colourless oil, which has only a slight odour, and boils at 150—155°

under 11 mm. pressure. A crystalline *polymeride*,  $(C_7H_{12}O)_x$ , is formed by the action of sulphuric acid on the aldehyde; it crystallises from ethyl acetate in needles and melts at 195—196° or, after resolidifying, at 202—203°.

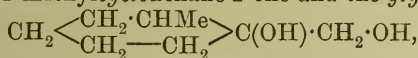
The *nitrosochloride* of methylenecyclohexane,  $(C_7H_{12}ONCl)_2$ , reacts with piperidine forming the crystalline *nitrolamine*,  $C_7H_{12}(NO) \cdot C_5H_{10}N$ , which melts at 127°. Elimination of hydrogen chloride from the nitrosochloride leads to the formation of a viscous *oxime*,  $C_7H_{10} \cdot NOH$ , which, when hydrolysed with dilute sulphuric acid, yields  $\Delta^1$ -*tetrahydrobenzaldehyde* (*cyclohexenealdehyde*),  $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH} \end{smallmatrix} > C \cdot COH$ . This

is obtained as an oil which has an odour resembling that of benzaldehyde, and forms a *semicarbazone*,  $C_8H_{13}ON_3$ , melting at 212—213°. Oxidation of the aldehyde by means of silver oxide leads to the formation of  $\Delta^1$ -*tetrahydrobenzoic acid*.

[With ERICH BESCHKE.]—2-Methylcyclohexane-1-ol-1-acetic acid,  $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} > C(OH) \cdot CH_2 \cdot CO_2H$ , is formed by condensing 1-methylcyclohexane-2-one with ethyl bromoacetate in presence of zinc and hydrolysing the resulting ester; it melts at 67—68°. When heated with sodium hydrogen sulphite at 160—170°, the ethyl ester loses water, forming the *ethyl ester* of the unsaturated acid. 1-Methyl- $\Delta^1$ -cyclohexene-2-acetic acid is obtained as an oil, which, when distilled, decomposes and yields 1-methyl-2-methylenecyclohexane,



This is obtained in a yield of 84 per cent. of the theoretical, boils at 122—125°, has a sp. gr. 0.808 and  $n_D$  1.4516 at 22°, and is oxidised by permanganate to 1-methylcyclohexane-2-one and the *glycol*,



melting at 59—60°. Hexahydro-*o*-tolualdehyde is obtained only in small quantities when the glycol is heated with dilute acids. The *semicarbazone*,  $C_9H_{17}ON_3$ , crystallises from boiling water and melts at 136—137°.

The *nitrosochloride* of 1-methyl-2-methylenecyclohexane is solid; the *nitrolamine* formed with piperidine is obtained as a syrup. When heated with dilute sulphuric acid, the *oxime* obtained from the nitrosochloride yields  $\Delta^1$ -*tetrahydro-*o*-tolualdehyde*, which forms a crystalline *semicarbazone* melting at 208—212°.

The behaviour of 3-methylcyclohexeneacetic acid (Abstr., 1901, i, 156; Tétry, Abstr., 1902, i, 584) is in accordance with the constitution  $CH_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} > C : CH \cdot CO_2H$ . The amide is now found to melt at 153—154°; when heated with phosphoric oxide, it forms the *nitrile*,  $C_8H_{13} \cdot CN$ , which boils at 108—112° under 10 mm., or at 230—234° under the atmospheric pressure, and has an odour resembling that of benzonitrile. With bromine in chloroform solution, the acid forms a crystalline *dibromide*,  $C_9H_{14}O_2Br_2$ , which melts at 127—129°, and when dissolved in an aqueous alkali carbonate gradually yields an oil having the properties of a monobromo-unsaturated com-



pound. 1-Methyl-3-methylenecyclohexane,  $\text{CH}_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{C} : \text{CH}_2$ , formed by slow distillation of 3-methylcyclohexeneacetic acid, boils at  $123-124^\circ$ , has a sp. gr.  $0.794-0.797$ ,  $n_D$   $1.4466$  at  $18^\circ$  or  $1.4461$  at  $20^\circ$ , and  $[\alpha]_D -29^\circ$  to  $-30.22^\circ$ , and when oxidised yields 1-methylcyclohexane-3-one and the glycol,  $\text{CH}_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ . This is obtained as a viscid mass, which boils at  $150-153^\circ$  under 39 mm. pressure, and when heated with dilute acids yields hexahydro-*m*-tolualdehyde.

The nitrosochloride of 1-methyl-3-methylenecyclohexane,  $(\text{C}_8\text{H}_{14}\text{ONCl})_2$ , is obtained in a yield of 15—20 per cent. of the theoretical, and with piperidine forms the nitrolamine,  $\text{C}_8\text{H}_{14}(\text{NO}) \cdot \text{C}_5\text{H}_{10}\text{N}$ , melting at  $136-137^\circ$ . The oxime of  $\Delta^1$ -tetrahydro-*m*-tolualdehyde is formed from the nitrosochloride by the action of alcoholic potassium hydroxide. The semicarbazone,  $\text{C}_9\text{H}_{15}\text{ON}_3$ , melts at  $206-207^\circ$ .

[With EDGAR EVANS.]—4-Methylcyclohexane-1-ol-1-acetic acid,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , formed by condensing 1-methylcyclohexane-4-one with methyl bromoacetate and hydrolysing the resulting ester, crystallises from dilute alcohol or boiling water in two forms, of which the one obtained in the greater amount melts at  $139.5-140.5^\circ$ , whilst the other melts at  $88-90^\circ$ . 4-Methylcyclohexene-1-acetic acid melts at  $42-43^\circ$  and boils at  $137-138^\circ$  under 14 mm. pressure; the silver salt,  $\text{C}_9\text{H}_{13}\text{O}_2\text{Ag}$ , was analysed. 1-Methyl-4-methylenecyclohexane,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C} : \text{CH}_2$ , boils at  $122-123^\circ$  and has a sp. gr.  $0.7925$  and  $n_D$   $1.4446$  at  $22^\circ$ . The glycol,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , crystallises readily, melts at  $87-88^\circ$ , and when heated with dilute acids yields principally a high boiling condensation product and a volatile oil which does not form a semicarbazone, together with only a small amount of hexahydro-*p*-tolualdehyde. The semicarbazone of this melts at  $154-156^\circ$ .

The nitrosochloride of 1-methyl-4-methylenecyclohexane is obtained in only a small yield; the nitrolamine formed with piperidine melts at  $134-135^\circ$ .  $\Delta^1$ -Tetrahydro-*p*-tolualdehyde, obtained through the oxime from the nitrosochloride, forms a semicarbazone melting at  $192-194^\circ$ .

G. Y.

Reduction of Partially Hydrogenated Benzenes. AUGUST KLAGES and FRITZ SOMMER (*Ber.*, 1906, 39, 2306—2315).—The hydrocarbon,  $\text{C}_{11}\text{H}_{16}$ , obtained by Rupe and Leichtenhan (this vol., i, 374) is more readily prepared by treating the reaction-product of carvone and magnesium methyl bromide with 40 per cent. sulphuric acid at  $-5^\circ$ ; it is regarded as 2-methyl- $\Delta^{2,6,8(9)}$ -menthatriene on account of its conversion into 2-methyl-*p*-cymene by a boiling 2 per cent. solution of hydrogen chloride in glacial acetic acid. 2-Methyl-*p*-cymene is a colourless, mobile liquid with the odour of cymene; it boils at  $86-87.5^\circ$  under 16 mm. and at  $198^\circ$  under 732 mm. pressure, is converted into tetra-

bromo-*o*-xylene by cold bromine and aluminium, and on treatment with fuming sulphuric acid yields two sulphonic acids, the  $\alpha$ -acid, the chloride of which is solid and forms a *sulphonanilide*,  $C_{17}H_{21}O_2NS$ , melting at  $186-187^\circ$ , and the  $\beta$ -acid, the chloride of which is an oil, and the *anilide*, a crystalline solid which melts at  $135-136^\circ$ .

*2-Methyl- $\Delta^{6,8(9)}$ -menthadiene-2-ol* (*2-methylcarveol*) is prepared by adding the reaction product of magnesium methyl bromide and carvone, after keeping for one hour, to an ice-cold concentrated solution of ammonium chloride; it is obtained quantitatively as a colourless oil with a faint odour, which boils at  $111^\circ$  under 14 mm. pressure, has a sp. gr.  $0.9471$  at  $20.4/4^\circ$ ,  $n_D$   $1.4911$ , and  $[\alpha]_D$   $36.08^\circ$  at  $20.4^\circ$ , and is changed by anhydrous oxalic acid at  $125^\circ$  into *2-methyl-p-cymene*.

*2-Ethyl- $\Delta^{6,8(9)}$ -menthadiene-2-ol* (*2-ethylcarveol*), prepared in similar manner, is a colourless oil which boils at  $118.5-119.5^\circ$  under 14 mm. pressure, has a sp. gr.  $0.9302$  at  $21^\circ/4^\circ$ ,  $n_D$   $1.4879$ , and  $[\alpha]_D$   $31.17^\circ$  at  $21^\circ$ .

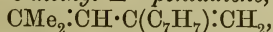
*2-Ethyl- $\Delta^{2,6,8(9)}$ -menthatriene*, obtained in similar manner to the methyl compound, is a colourless, mobile oil which boils at  $100-101^\circ$  under  $13.5$  mm. pressure, has a sp. gr.  $0.8859$  at  $18^\circ/4^\circ$ ,  $n_D$   $1.5041$ , and  $[\alpha]_D$   $86.19^\circ$  at  $18^\circ$ , and is converted by 2 per cent. hydrogen chloride in glacial acetic acid into *2-ethylcymene*,  $C_{12}H_{18}$ , a colourless oil which boils at  $103^\circ$  under 19 mm. and at  $214^\circ$  under 754 mm. pressure, has a sp. gr.  $0.8665$  at  $21.1^\circ/4^\circ$ ,  $n_D$   $1.4965$  at  $21.1^\circ$ , is easily soluble in sulphuric acid, and is converted by bromine and aluminium into *pentabromotoluene*, which forms long, colourless needles and melts at  $283^\circ$ .

*2-Phenyl- $\Delta^{6,8(9)}$ -menthadiene-2-ol* (*2-phenylcarveol*) is a colourless oil which boils at  $159-160^\circ$  under 12 mm. pressure, has a sp. gr.  $1.0156$  at  $15.1^\circ/4^\circ$ ,  $n_D$   $1.5562$ , and  $[\alpha]_D$   $81.42^\circ$  at  $15.1^\circ$ .

*2-Phenyl- $\Delta^{2,6,8(9)}$ -menthatriene*, containing a little *2-phenyl-p-cymene*, boils at  $152-153^\circ$  under 13 mm. pressure, has a sp. gr.  $0.9882$  at  $13.8^\circ/4^\circ$ ,  $n_D$   $1.5631$ , and  $[\alpha]_D$   $110.2^\circ$  at  $13.8^\circ$ , and is converted by hydrogen chloride in glacial acetic acid into *2-phenyl-p-cymene*, which can also be obtained from *2-phenylcarveol* by anhydrous oxalic acid at  $120^\circ$  or by hydrogen chloride and pyridine at  $140^\circ$ ; it is a highly refractive, colourless oil which boils at  $268^\circ$  under 752 mm., or at  $153-154^\circ$  under 14 mm. pressure, has a sp. gr.  $0.9822$  at  $13.8^\circ/4^\circ$ ,  $n_D$   $1.5670$  at  $13.8^\circ$ , and readily forms a sulphonic acid with fuming sulphuric acid.

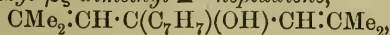
C. S.

**Action of Magnesium Benzyl Chloride on Mesityl Oxide and Phorone.** THEODOR VON FELLEBERG (*Ber.*, 1906, 39, 2064—2066. Compare *Abstr.*, 1904, i, 961).— $\beta$ -Hydroxy- $\beta$ -benzyl- $\delta$ -methyl- $\Delta^7$ -pentene,  $CMe_2:CH:C(C_7H_7)Me\cdot OH$ , prepared from mesityl oxide, is a faintly yellow, somewhat viscous liquid with an agreeable odour; it is slightly volatile in steam, and by distillation under the ordinary pressure yields  $\beta$ -benzyl- $\delta$ -methyl- $\Delta^7$ -pentadiene,



which is a colourless, mobile liquid with an odour of dimethylpentadiene; it boils at  $234-236^\circ$  under 730 mm. pressure.

$\delta$ -Hydroxy- $\delta$ -benzyl- $\beta\zeta$ -dimethyl- $\Delta^{8\epsilon}$ -heptadiene,



obtained from phorone, is a viscous, faintly yellow liquid with a pleasant aromatic odour; it is slightly volatile in steam, and by distillation, even under 12 mm. pressure, loses water, forming  $\delta$ -benzylidene- $\beta\zeta$ -dimethyl- $\Delta^{\beta\epsilon}$ -heptadiene,  $\text{CMe}_2\cdot\text{CH}\cdot\text{C}(\text{CHPh})\cdot\text{CH}\cdot\text{CMe}_2$ , which, after repeated distillation, is obtained as a nearly colourless, mobile liquid boiling at  $277\text{--}278^\circ$  under 724 mm. pressure. C. S.

**Oxidation of Diphenyl Diselenide.** M. STOECKER and FRIEDRICH KRAFFT (*Ber.*, 1906, 39, 2197—2201. Compare Krafft and Lyons, *Abstr.*, 1896, i, 304).—The nitrate of phenylselenious acid melts and detonates at about  $112^\circ$ ; when dissolved in water, neutralised with ammonia, and treated with silver nitrate, it yields *silver phenylselenite*,  $\text{SePhO}_2\text{Ag}$ , which is obtained as a crystalline precipitate. The *barium*,  $(\text{SePhO}_2)_2\text{Ba}$ , and *copper*,  $(\text{SePhO}_2)_2\text{Cu}$ , salts are described. The free acid,  $\text{SePhO}_2\text{H}\cdot\text{H}_2\text{O}$  or  $\text{SePh}(\text{OH})_3$ , prepared by the action of  $N/10$  hydrochloric acid on the silver salt, forms a white, crystalline mass, melts at  $122\text{--}124^\circ$ , loses  $\text{H}_2\text{O}$  at  $100\text{--}130^\circ$  under 15 mm. pressure, and then melts and decomposes at  $170^\circ$ . On reduction with zinc and hydrochloric acid, it forms *phenyl hydrogen selenide*,  $\text{SeHPh}$ , which boils at  $183^\circ$  and is oxidised by air, forming diphenyl diselenide.

The oxidation of diphenyl diselenide by chlorine in aqueous solution at  $50^\circ$  leads to the formation of *phenylselenic acid*,  $\text{SePhO}_3\text{H}$ , which is isolated in the form of its white, crystalline *silver salt*,  $\text{SePhO}_3\text{Ag}$ ; this detonates feebly when heated. The *barium*,  $(\text{SePhO}_3)_2\text{Ba}$ ; *copper*,  $(\text{SePhO}_3)_2\text{Cu}$ ; and *cadmium*,  $(\text{SePhO}_3)_2\text{Cd}$ , salts are described. The free acid is obtained as a hygroscopic syrup, which is stable when dried at  $105^\circ$ , detonates at  $180\text{--}190^\circ$ , forming phenyl diselenide, phenyl selenide, and free selenium, and in moist air forms a *hydrate*, crystallising in glistening prisms. The acid is reduced by concentrated hydrochloric acid, forming phenylselenious acid.

Both these acids deposit red selenium more or less quickly when exposed to light. G. Y.

**Alkaloidal Salts of *i*-sec-butylbenzenesulphonic Acid.** AUGUST KLAGES (*Ber.*, 1906, 39, 2131—2135).—Since Klages and Sautter have shown (*Abstr.*, 1904, i, 302) that optically active benzene hydrocarbons can be formed from their sulphonic acids without undergoing racemisation, the author has attempted to resolve *r*-sec-butylbenzenesulphonic acid into its optically active components by the aid of alkaloids. The results were negative.

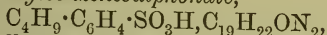
*sec*-Butylbenzene,  $\text{CHMeEtPh}$ , is sulphonated and converted into the barium sulphonate, which, by the action of phosphorus pentachloride, yields *sec-butylbenzenesulphonic chloride* as a colourless oil, which boils at  $179\text{--}180^\circ$  under 20 mm. pressure and has a sp. gr.  $1.202$  at  $16.4^\circ/4^\circ$ ; the *anilide* melts at  $63\text{--}64^\circ$  and the *sulphonamide* at  $80\text{--}81^\circ$ .

*Quinine sec-butylbenzenesulphonate*,  $\text{C}_4\text{H}_9\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}\cdot\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$ , prepared by the addition of quinine sulphate to barium *sec*-butylbenzenesulphonate, is sparingly soluble in water, from which it separates in needles. When dried at  $110^\circ$ , it melts at  $184^\circ$  and



has  $[\alpha]_D -10.5^\circ$  at  $20^\circ$  in methyl-alcoholic solution ( $c=1.238$ ). It was not found possible to separate it into two isomeric quinine salts.

*Cinchonidine sec-butylbenzenesulphonate*,

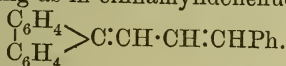


forms glistening needles and, when dried at  $110^\circ$ , melts at  $205^\circ$ . It has  $[\alpha]_D -7.34^\circ$  at  $20^\circ$  in methyl-alcoholic solution ( $c=1$ ). The brucine salt is oily.

*Strychnine sec-butylbenzenesulphonate*,  $C_4H_9 \cdot C_6H_4 \cdot SO_3H, C_{21}H_{22}O_2N_2$ , separates from benzene in needles, melts at  $189-190^\circ$ , and in methyl-alcoholic solution ( $c=0.846$ ) is optically inactive.

A. McK.

**Derivatives of Fulvene. I. Condensation of Indene with Aldehydes.** JOHANNES THIELE and ADOLF BÜHNER (*Annalen*, 1906, 347, 249—274. Compare Thiele, *Abstr.*, 1900, i, 298; 1901, i, 76; Kipping and Hall, *Trans.*, 1900, 77, 471; Marckwald, *Abstr.*, 1900, i, 434).—The ethylene linking lying outside of the ring of fulvene derivatives is readily reduced by aluminium amalgam in moist ethereal solution if a hydrogen atom of the methylene group is substituted by phenyl or carboxyl. The phenyl group may be attached by an intermediate ethylene linking as in cinnamylidenefluorene,



Whilst bisdiphenylene-ethylene is reduced to bisdiphenylene-ethane (compare De la Harpe and van Dorp, *Abstr.*, 1876, i, 242), tetraphenylethylene is not reduced by aluminium amalgam.

1-Benzylindene,  $CH_2 < \begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ CH \end{array} > C \cdot CH_2Ph$ , formed by reducing benzyl-

ideneindene, is obtained as an almost colourless oil, which boils at  $183-185^\circ$  under 13 mm. pressure, is oxidised slowly by air, becoming yellow, gives a yellow coloration with concentrated sulphuric acid, and forms with bromine a *dibromide*, and with amyl nitrite and hydrochloric acid a solid, unstable *nitrosochloride*. It condenses with benzaldehyde in presence of methyl-alcoholic potassium hydroxide, forming 1-benzyl-

3-benzylideneindene,  $CHPh:C < \begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ CH \end{array} > C \cdot CH_2Ph$  (compare *Abstr.*, 1901, i, 76). This crystallises from alcohol in glistening, yellow leaflets, melts at  $137-137.5^\circ$ , and gives a violet coloration with concentrated sulphuric acid. It is formed also by distillation at  $250-260^\circ$  under 12 mm. pressure of the colourless hydrocarbon obtained previously (*Abstr.*, 1901, i, 76) by reduction of chlorobenzylbenzylidene-

indene,  $CHPh:C < \begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ CH \end{array} > C \cdot CHClPh$ . The results of ebullioscopic molecular weight determinations with the colourless hydrocarbon agree with the formula  $C_{23}H_{18}$ .

1:3-Dibenzylindene,  $CH_2Ph \cdot C < \begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ CH \end{array} > CH \cdot CH_2Ph$ , is formed by reduction of benzylbenzylideneindene; it crystallises from light petroleum in stout, colourless prisms, or from methyl alcohol in white leaflets, melts at  $62-63^\circ$ , when treated with amyl nitrite and hydrochloric acid forms an unstable *nitrosochloride*, and reacts with bromine

in chloroform solution, forming a *dibromide*,  $C_{23}H_{20}Br_2$ , which separates from light petroleum in stout, colourless crystals and melts and decomposes at  $103-104^\circ$ . When boiled with pyridine, the dibromide loses  $2HBr$ , forming benzylbenzylideneindene.

On preparing Marckwald's viscid benzylindene (*loc. cit.*) and distilling the product in a vacuum, the authors obtained a large fraction which is identical with the product of the reduction of benzylideneindene.

Marckwald's 1-methylindene has been compared and found to be identical with Roser's 3-methylindene (Abstr., 1888, 1303).

3-Benzylidene-1-methylindene,  $CMe \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C:CHPh$  (compare

Marckwald, *loc. cit.*), is prepared by the condensation of methylindene with benzaldehyde; it crystallises from methyl alcohol, melts at  $43-44^\circ$ , and gives a reddish-violet coloration with concentrated sulphuric acid. On reduction, it yields 3-benzyl-1-methylindene (?) as a colourless oil, which combines with 1 mol. of bromine, but does not form condensation products.

3-Anisylidene-1-methylindene,  $CMe \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C:CH \cdot C_6H_4 \cdot OMe$ ,

formed by the condensation of methylindene with anisaldehyde, crystallises from alcohol in glistening, yellow leaflets, melts at  $113^\circ$ , and gives a violet-blue coloration with concentrated sulphuric acid.

The action of anisaldehyde on indene in presence of methyl-alcoholic potassium hydroxide leads to the formation of anisylideneindene and hydroxyanisylanisylideneindene, which are separated by fractional crystallisation from alcohol.

1-Anisylideneindene,  $CH \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C:CH \cdot C_6H_4 \cdot OMe$ , is obtained as a reddish-yellow, crystalline powder, melts at  $118-119^\circ$ , and gives a greenish-brown coloration with concentrated sulphuric acid. When reduced with aluminium amalgam, it yields 1-anisylindene,  $CH_2 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C:CH_2 \cdot C_6H_4 \cdot OMe$ , which crystallises in white leaflets, melts at  $63-64^\circ$ , and condenses with anisaldehyde, forming 3-anisyl-1-anisylideneindene,

$OMe \cdot C_6H_4 \cdot CH_2 \cdot C \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C:CH \cdot C_6H_4 \cdot OMe$ ,

crystallising in yellow leaflets and melting at  $111-112^\circ$ .

*$\alpha$ -Hydroxyanisylanisylideneindene,*

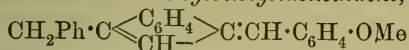
$OMe \cdot C_6H_4 \cdot CH(OH) \cdot C \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C:CH \cdot C_6H_4 \cdot OMe$ ,

crystallises from benzene in small, lemon-yellow leaflets, melts at  $141.5-142.5^\circ$ , gives a bluish-green coloration with concentrated sulphuric acid, and on reduction yields  *$\alpha$ -hydroxydianisylindene*,

$OMe \cdot C_6H_4 \cdot CH(OH) \cdot CH \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C:CH_2 \cdot C_6H_4 \cdot OMe$ . This separates

from a mixture of alcohol and ether as a colourless, flocculent substance melting at  $175-178^\circ$ , or from alcohol in a vacuum as a colourless, viscid oil, and when treated with alcoholic potassium hydroxide is converted into anisylanisylideneindene.

*Benzylanisylideneindene* or *anisylbenzylideneindene*,



or  $\text{CHPh} : \text{C} \begin{array}{c} \nwarrow \text{C}_6\text{H}_4 \\ \nearrow \text{CH} \end{array} > \text{C} : \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , is formed by the action of anisaldehyde on benzylindene or of benzaldehyde on anisylindene; it crystallises from alcohol, melts at 132—133°, and gives an indigo-blue coloration with concentrated sulphuric acid. The identity of the products of the two methods of formation is explained by assuming an oscillation of the ethylene linking (compare Knorr, Abstr., 1894, i, 543; Fischer and Rigaud, Abstr., 1902, i, 188).

*p-Nitro- $\alpha$ -hydroxybenzyl-p-nitrobenzylideneindene*,



prepared by the condensation of indene with *p*-nitrobenzaldehyde in presence of a small quantity of an alkali hydroxide, forms yellow crystals and melts and decomposes at 216—217°.

The reduction of hydroxybenzylbenzylideneindene with aluminium amalgam in moist ethereal solution leads to the formation of the colourless isomeride of benzylbenzylideneindene, together with *hydroxy-dibenzylindene*,  $\text{OH} \cdot \text{CHPh} \cdot \text{CH} \begin{array}{c} \nwarrow \text{C}_6\text{H}_4 \\ \nearrow \text{CH} \end{array} > \text{C} : \text{CH}_2\text{Ph}$ , which is obtained as a viscid oil. When distilled in a vacuum, it decomposes, yielding benzaldehyde, benzylbenzylideneindene, and a brown resin, and when treated with alcoholic potassium hydroxide loses water, forming benzylbenzylideneindene.

The residues from the commercial indene used in the above condensations, after complete removal of the indene, yielded an oil which boiled at the same temperature as indene, and on analysis gave figures pointing to the presence of coumarone together with a small amount of hydroindene (compare Weger and Billmann, Abstr., 1903, i, 332).

G. Y.

**Derivatives of Fulvene. III. Condensation Products of Fluorene.** JOHANNES THIELE and FRANZ HENLE (*Annalen*, 1906, 347, 290—315. Compare preceding abstract).—The reactivity of the methylene group of fluorene is less than that of indene, which is itself less reactive than *cyclopentadiene*, that is, the activity decreases as the ethylene linkings of the five-atom ring are rendered inactive by benzene nuclei. The colour of these three substances diminishes in the same order.

Fluorene does not react with aliphatic aldehydes, or with ketones, or with amyl nitrite and sodium ethoxide, but forms condensation products with aromatic aldehydes in presence of alcoholic alkali hydroxides. These products form additive compounds with bromine, and are reduced by aluminium amalgam and moist ether, yielding hydrocarbons of which those having an ethylene linking in the  $\alpha$ -position to a phenyl group form additive compounds with picric acid.

Benzylidenefluorene (Abstr., 1900, i, 347) crystallises in rhombic



prisms [ $a:b:c = 0.9942:1:2.6859$ ], is less soluble than fluorene in organic solvents, and decolorises potassium permanganate in sodium carbonate solution. The *picrate*,  $C_{20}H_{14}C_6H_3O_7N_3$ , crystallises in orange needles, melts at  $115-116^\circ$ , and is decomposed by water. The

*dibromide*,  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > CBr \cdot CHBrPh$ , forms glistening prisms, melts at  $112^\circ$ , and on treatment with zinc dust and glacial acetic acid yields benzylidenefluorene.

*Benzylfluorene*,  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > CH \cdot CH_2Ph$ , formed by reduction of the benzylidene compound with sodium and amyl alcohol, or in better yield by means of aluminium amalgam, crystallises from light petroleum, melts at  $130-131^\circ$ , and gives with concentrated sulphuric acid a violet coloration, becoming blue and finally disappearing on addition of water.

The action of benzyl chloride and potassium hydroxide on fluorene in a sealed tube at  $270^\circ$ , or on benzylfluorene at  $230^\circ$ , leads to the formation of dibenzylfluorene, which is identical with Weissgerber's supposed benzylfluorene (Abstr., 1901, i, 521). It crystallises in thin prisms and melts at  $147-148^\circ$ .

*Anisylidenefluorene*,  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:CH \cdot C_6H_4 \cdot OMe$ , crystallises from glacial acetic acid or ethyl acetate in stout, yellow prisms, melts at  $128-129^\circ$ , is resinified by sulphuric acid and zinc chloride, and on reduction yields *anisylfluorene*,  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > CH \cdot CH_2 \cdot C_6H_4 \cdot OMe$ . This crystallises from light petroleum in plates and melts at  $108-108.5^\circ$ .

*Furfurylidenefluorene*,  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:CH \cdot C_4H_3O$ , crystallises from alcohol in yellow needles. *Furfurylfluorene*,  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > CH \cdot CH_2 \cdot C_4H_3O$ , crystallises in stout, colourless, rhombic prisms and melts at  $91-92^\circ$ .

Bisdiphenylene-ethane, formed by reduction of bisdiphenylene-ethylene with aluminium amalgam, melts at  $239-240^\circ$  (De la Harpe and van Dorp, Abstr., 1876, i, 242).

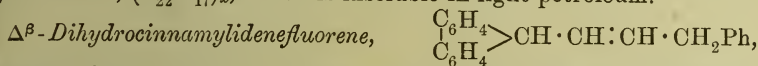
*Cinnamylidenefluorene*,  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:CH \cdot CH:CHPh$ , is prepared by the action of cinnamaldehyde and sodium ethoxide on fluorene in absolute alcoholic solution at  $55^\circ$ ; it crystallises from glacial acetic acid in lemon-yellow needles and melts at  $154.5^\circ$ . The *picrate*,  $C_{22}H_{16} \cdot 2C_6H_3O_7N_3$ , crystallises in needles and melts at  $178-179^\circ$ .

The *picrate* of  $\alpha\delta$ -diphenyl- $\Delta\gamma$ -butadiene,  $C_{16}H_{14} \cdot 2C_6H_3O_7N_3$  (Thiele and Schleussner, Abstr., 1899, i, 612), crystallises in yellowish-red needles and melts at  $152-153^\circ$ .

*Cinnamylidenefluorene dibromide*,  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:CH \cdot CHBr \cdot CHBrPh$ , formed by the action of bromine on the hydrocarbon in chloroform solution, crystallises in yellow prisms or needles, melts and decomposes

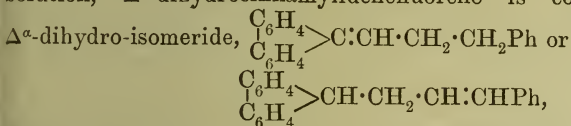
at 127°, is decomposed by solvents of high boiling point, and regenerates cinnamylidenefluorene when treated with zinc dust and glacial acetic acid at the ordinary temperature. When oxidised by means of chromic acid in glacial acetic acid solution at 25–30°, it yields dibromodihydrocinnamic acid and fluorenone. The *tetrabromide*,  $\text{C}_6\text{H}_4 > \text{CBr} \cdot [\text{CHBr}]_2 \cdot \text{CHBrPh}$ , is formed by the action of bromine on cinnamylidenefluorene in chloroform solution exposed to bright sunshine; it forms sheaves of crystals, melts and decomposes at about 160°, and yields cinnamylidenefluorene when treated with zinc dust and glacial acetic acid.

The reduction of cinnamylidenefluorene leads to the formation of bismonohydrocinnamylidenefluorene, which separates from the light petroleum extract of the reduction product,  $\Delta^\beta$ -dihydrocinnamylidenefluorene, which remains dissolved in the light petroleum, and a hydrocarbon,  $(\text{C}_{22}\text{H}_{17})_x$ , which is insoluble in light petroleum.



separates from alcohol in long, almost colourless, slightly shimmering crystals, melts at 88°, is readily soluble in acetone, ether, benzene, toluene, chloroform, or glacial acetic acid, does not form a picrate, reduces ammoniacal silver nitrate solution at the ordinary temperature, and gives with benzaldehyde and much concentrated sulphuric acid an intense red coloration which is destroyed by addition of water. The *dibromide*,  $\text{C}_{22}\text{H}_{18}\text{Br}_2$ , crystallises in matted needles, melts at 133°, and forms the  $\Delta^\beta$ -dihydro-compound when treated with zinc dust and glacial acetic acid, or when heated with methyl-alcoholic potassium hydroxide.

When boiled with sodium ethoxide or piperidine in alcoholic solution,  $\Delta^\beta$ -dihydrocinnamylidenefluorene is converted into the



which crystallises from alcohol in small, white leaflets, melts at 81–82°, and forms a *picrate*,  $\text{C}_{22}\text{H}_{18} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ . This crystallises in glistening, reddish-yellow needles and melts at 128–129°. The *dibromide*,  $\text{C}_{22}\text{H}_{18}\text{Br}_2$ , crystallises from light petroleum, melts at 94–96°, is decomposed by potassium hydroxide, and forms  $\Delta^\alpha$ -dihydrocinnamylidenefluorene when treated with zinc dust and glacial acetic acid.

*Bismonohydrocinnamylidenefluorene*,  $(\text{C}_{22}\text{H}_{17})_2$ , separates from light petroleum in crystals containing petroleum and melting at about 120°, from acetone in crystals containing acetone and melting at 112–115°, or from glacial acetic acid in glistening crystals,  $\text{C}_{44}\text{H}_{34} \cdot \text{C}_2\text{H}_4\text{O}_2$ , melting at 124°. The hydrocarbon melts at 160–161° and is readily soluble in hot acetone, benzene, toluene, or chloroform.

The *hydrocarbon*,  $(\text{C}_{22}\text{H}_{17})_x$ , crystallises from nitrobenzene, melts at 257° (corr.), and evolves hydrogen bromide when heated with bromine.

G. Y.

**New Method for the Preparation of Tetraphenylmethane.** MARTIN FREUND (*Ber.*, 1906, 39, 2237—2238).—Tetraphenylmethane is one of the products resulting from the action of magnesium phenyl bromide on triphenylmethyl bromide; triphenylmethyl peroxide is also formed. A. McK.

**Organic Double Salts with Bismuth Chloride.** LUDWIG VANINO and F. HARTL (*Arch. Pharm.*, 1906, 244, 216—220).—Compounds of bismuth chloride with the following bases were obtained by mixing the constituents in acetone, alcohol, or ether solution. They are crystalline; and some are, others are not, decomposed by water.

*Diphenylamine*,  $\text{NHPh}_2, \text{BiCl}_3$ . *Nitrosodiphenylamine*,

$\text{NO} \cdot \text{NPh}_2, \text{BiCl}_3$ .

*Nitrosodimethylaniline*,  $2\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2, 3\text{BiCl}_3$ . *Aldehyde-ammonia* (really a compound with a polymeric ethylideneimine),

$(\text{CHMe} \cdot \text{NH})_3, 3\text{BiCl}_3$ .

*Methylamine hydrochloride*,  $3\text{NH}_3\text{MeCl}, 2\text{BiCl}_3$ . *Rheumatine*,

$\text{C}_{34}\text{H}_{34}\text{O}_7\text{N}_2, 2\text{BiCl}_3$ .

*Quinaphenine*,  $2\text{C}_{27}\text{H}_{29}\text{O}_3\text{N}_3, 5\text{BiCl}_3$ . *Piperazine*,  $2\text{C}_4\text{H}_{10}\text{N}_2, 3\text{BiCl}_3$ .

C. F. B.

**Formation of Bases from Acetophenone, Formaldehyde, and Ammonium Chloride.** H. SCHÄFER and BERNHARD TOLLENS (*Ber.*, 1906, 39, 2181—2189. Compare Marle and Tollens, *Abstr.*, 1903, i, 493; Tollens, *Abstr.*, 1904, i, 507).—The action of formaldehyde and ammonium chloride on acetophenone leads to the formation of *s*-triphenacylomethylamine, *s*-diphenacylomethylamine, and possibly phenacylomethylamine hydrochlorides.

*s*-Triphenacylomethylamine hydrochloride,  $\text{N}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{COPh})_3, \text{HCl}$ , is extracted from the cold reaction product by means of chloroform; it crystallises in white, microscopic needles, melts at 200—201°, and in dilute alcoholic solution forms precipitates with the alkaloid reagents. The free base,  $\text{N}(\text{C}_9\text{H}_9\text{O})_3, \frac{1}{2}\text{H}_2\text{O}$ , crystallises from ether in monoclinic needles. The *sulphate*,  $2\text{N}(\text{C}_9\text{H}_9\text{O})_3, \text{H}_2\text{SO}_4$ , melts at 180—181°; the *nitrate*,  $\text{N}(\text{C}_9\text{H}_9\text{O})_3, \text{HNO}_3, \frac{1}{2}\text{H}_2\text{O}$ , forms microscopic needles and melts at 142—143°; the *platinichloride*,  $(\text{C}_{27}\text{H}_{27}\text{O}_3\text{N})_2, \text{H}_2\text{PtCl}_6$ , forms a dark yellow, crystalline precipitate and melts at 207°. When boiled with aqueous hydroxylamine in a reflux apparatus, the base evolves ammonia and yields an oil smelling of cinnamaldehyde. In one case, a substance melting at 228° was obtained by boiling the hydrochloride of the base with hydroxylamine hydrochloride in alcoholic solution. With phenylhydrazine, the base forms the phenylhydrazone of phenylvinyl ketone (Moureu, *Abstr.*, 1894, i, 30), which crystallises in yellow, monoclinic needles, melts at 152—153°, and dissolves in ether, light petroleum, or benzene, forming solutions with deep blue fluorescence. Phenyl vinyl ketone is formed when *s*-triphenacylomethylamine hydrochloride is distilled in a current of steam.

The action of phenylhydrazine on the dibromide of phenyl vinyl ketone leads to the formation of phenylhydrazine hydrobromide.

*s*-Diphenacylomethylamine hydrochloride,  $\text{NH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{COPh})_2, \text{HCl}$ , remains in the distillation residue when *s*-triphenacylomethylamine-

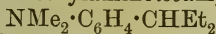


hydrochloride is heated in a current of steam. It forms a white, crystalline mass, melts when not pure at 136—138°, and forms a *platinichloride*,  $(C_{18}H_{19}O_2N)_2, H_2PtCl_6$ , melting at about 155°.

G. Y.

**Dialkylaminobenzaldehydes.** IV. FRANZ SACHS and FRANZ MICHAELIS (*Ber.*, 1906, **39**, 2163—2171. Compare Sachs and Steinert, *Abstr.*, 1904, i, 506; F. and L. Sachs, *Abstr.*, 1905, i, 202).—*Trinitro-p-dimethylaminoisopropylbenzene*,  $C_{11}H_{14}N(NO_2)_3$ , prepared by nitrating dimethylamino-*p-isopropylbenzene*,  $NMe_2 \cdot C_6H_4 \cdot CHMe_2$ , formed by the action of magnesium methyl iodide on *p*-dimethylaminobenzaldehyde (Sachs and Sachs, *loc. cit.*), separates from dilute alcohol in bluish-yellow needles and melts at 112°.

*Trinitro-p-dimethylaminoisoomylbenzene*,  $NMe_2 \cdot C_6H(NO_2)_3 \cdot CHEt_2$ , prepared by nitrating *p*-dimethylaminoisoomylbenzene,



(Sachs and Sachs, *loc. cit.*), separates from alcohol in yellow, hexagonal crystals and melts at 65°.

*p-Dimethylaminoisoeptylbenzene*,  $NMe_2 \cdot C_6H_4 \cdot CHPr_2$ , prepared by the action of magnesium propyl bromide on *p*-dimethylaminobenzaldehyde, is a yellow oil and boils at 164° under 24 mm. pressure.

*p-Dimethylaminophenyldiisobutylmethane*,  $NMe_2 \cdot C_6H_4 \cdot CH(C_4H_9)_2$ , prepared from magnesium butyl iodide and *p*-dimethylaminobenzaldehyde, is a yellow oil which boils at 236° under 13 mm. pressure. It gives a reddish-brown coloration with potassium dichromate and sulphuric acids.

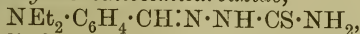
*p-Dimethylaminophenyldibenzylmethane*,  $NMe_2 \cdot C_6H_4 \cdot CH(CH_2Ph)_2$ , prepared from magnesium benzyl chloride and *p*-dimethylaminobenzaldehyde, separates from dilute alcohol in tetragonal prisms and melts at 82°. It gives a dark red coloration with potassium dichromate and sulphuric acid.

*p-Dimethylaminophenyldinaphthylmethane*,  $NMe_2 \cdot C_6H_4 \cdot CH(C_{10}H_7)_2$ , prepared from magnesium  $\alpha$ -naphthyl bromide and *p*-dimethylaminobenzaldehyde, crystallises from carbon disulphide in snow-white needles and melts at 223°.

*p-Diethylaminoisopropylbenzene*,  $NEt_2 \cdot C_6H_4 \cdot CHMe_2$ , prepared from magnesium methyl iodide and *p*-diethylaminobenzaldehyde, is a yellow oil and boils at 156° under 43 mm. pressure.

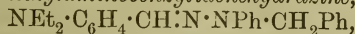
*p-Diethylaminoisoeptylbenzene*,  $NEt_2 \cdot C_6H_4 \cdot CHPr_2$ , prepared from magnesium propyl bromide and *p*-diethylaminobenzaldehyde, is a yellow oil and boils at 165° under 22 mm. pressure.

*p-Diethylaminobenzylidenethiosemicarbazide*,



prepared from *p*-diethylaminobenzaldehyde and thiosemicarbazide, forms tetragonal prisms and melts at 180°.

*Phenylbenzyl-p-diethylaminobenzylidenehydrazine*,



prepared from *p*-diethylaminobenzaldehyde and phenylbenzylhydrazine, separates from alcohol in tetragonal prisms and melts at 123°.

*p-Diethylaminobenzylideneacetone*,  $NEt_2 \cdot C_6H_4 \cdot CH:CH \cdot COMe$ , prepared by the addition of acetone and a few drops of alkali to a solu-

tion of *p*-ethylaminobenzaldehyde in alcohol, separates in reddish-yellow, spear-shaped crystals and melts at 164°.

*p*-Diethylaminobenzylidenemalononitrile,  $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN})_2$ , prepared from *p*-diethylaminobenzaldehyde and malononitrile in presence of a little piperidine, separates from alcohol in yellowish-red, rhombic prisms and melts at 130°.

*p*-Diethylaminobenzylidenebenzyl cyanide,  $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CPh} \cdot \text{CN}$ , prepared from *p*-diethylaminobenzaldehyde and benzyl cyanide, crystallises from alcohol in yellow, prismatic needles, and melts at 97°.

*p*-Diethylaminobenzylidene-*p*-nitrobenzyl cyanide,  $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , prepared from *p*-diethylaminobenzaldehyde and *p*-nitrobenzyl cyanide, separates from glacial acetic acid in dark red needles and melts at 206°.

*p*-Diethylaminobenzylidenerrhodanic acid, 
$$\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C} \begin{array}{l} \text{CO} \cdot \text{CS} \\ \text{S} - \text{NH} \end{array}$$
, prepared from *p*-diethylaminobenzaldehyde and rhodanic acid, separates from alcohol in dark red needles and melts at 182°.

*p*-Diethylaminobenzylidenebarbituric acid, 
$$\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C} \begin{array}{l} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{array} > \text{CO}$$
, prepared from *p*-diethylaminobenzaldehyde and barbituric acid, separates from glacial acetic acid in red needles and melts at 129°.

*p*-Diethylaminobenzylidenecyanoacetamide,  $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2$ , prepared from *p*-diethylaminobenzaldehyde and cyanoacetamide in the presence of a little piperidine, separates from alcohol in orange, rhombic prisms and melts at 134·5°. A. McK.

Pseudo-acids. ARTHUR HANTZSCH (*Ber.*, 1906, 39, 2098—2112); HANS EULER (*ibid.*, 2265—2269).—Polemical (compare this vol., i, 415). C. S.

Imide Bromides and their Decomposition. JULIUS VON BRAUN and CARL MÜLLER (*Ber.*, 1906, 39, 2018—2022. Compare Abstr., 1904, i, 688, 731, 841, 918; 1905, i, 634, 636).—The imide bromides, prepared by the action of phosphorus pentabromide on fatty or aromatic amides, resemble the imide chlorides, but are more readily hydrolysed by moisture. Amides of aliphatic acids react energetically with phosphorus pentabromide, the final products being basic substances which do not form the amide when treated with water.

Benzanilide and phosphorus pentabromide interact, forming the imide bromide, which is obtained as a reddish-yellow, crystalline cake, decomposes when distilled, and with water forms benzanilide. Methylbenzamide, when mixed with phosphorus pentabromide at the ordinary temperature, forms the imide bromide, which, when slightly

heated, decomposes into methyl bromide and benzonitrile, a small residue containing cyaphenine remaining on distillation of the products. Similarly, benzylbenzamide yields benzyl bromide and benzonitrile. The imide bromides may be isolated if the reaction with phosphorus pentabromide is carried out in chloroform solution.

The action of phosphorus pentabromide on dibenzoylhexamethylenediamine and on dibenzoylheptamethylenediamine leads to the formation of  $\alpha\zeta$ -dibromohexane and  $\alpha\eta$ -dibromoheptane, which, on treatment with sodium phenoxide, yield  $\alpha\zeta$ -diphenoxyhexane and  $\alpha\eta$ -diphenoxyheptane respectively. G. Y.

**Action of Nitrous Acid on Tolyl- and *m*-Xylyl-carbamides and on Phenylthiocarbamide.** II. J. HAAGER and R. DOHT (*Monatsh.*, 1906, 27, 267—279. Compare Abstr., 1904, i, 236; Walther and Wlodkowsky, Abstr., 1899, i, 590).—Nitrous acid reacts with *m*- and *p*-tolylcarbamides in the same manner as with phenylcarbamide, forming the nitroso-derivatives in presence of a limited quantity, but the carbamides in presence of an excess, of hydrochloric acid. *o*-Tolyl- and *m*-xylyl-carbamides yield the corresponding carbimides, but not the nitroso-derivatives. Nitrous acid does not react with  $\alpha$ - and  $\beta$ -naphthylcarbamides in hydrochloric acid solution.

*m*-Tolylcarbimide,  $C_8H_7ON$ , boils at  $183^\circ$  and behaves towards water, absolute alcohol, and pyridine in the same manner as other carbimides.

Nitroso-*p*-tolylcarbamide melts and decomposes at  $85^\circ$  ( $83^\circ$ ; Walther and Wlodkowsky, *loc. cit.*).

*m*-Xylyl-4-carbimide,  $C_6H_3Me_2 \cdot NCO$ , formed from *m*-xylyl-4-carbamide by the action of nitrous acid in hydrochloric or of sodium nitrite in glacial acetic acid solution, is obtained as a yellow oil, which boils at  $215^\circ$  and is more stable than other carbimides towards water.

The acid filtrates from the preparation of the nitrosocarbamides and of the carbimides contain the corresponding diazonium chlorides.

Whilst the chief product of the interaction of nitrous acid and phenylthiocarbamide is dianilino-*o*-diazothiole, which melts at  $190^\circ$  ( $181^\circ$ ; Hector, Abstr., 1889, 872; 1890, 526), a portion of the thiocarbamide reacts with the nitrous acid in the same way as does phenylcarbamide, forming phenylcarbimide. G. Y.

**Constitution and Colour of Nitrophenols.** HUGO KAUFFMANN (*Ber.*, 1906, 39, 1959—1966. Compare Abstr., 1900, i, 480; 1901, i, 318).—The author criticises Hantzsch's views (this vol., i, 353) and concludes that whilst the "quinone theory" of colour explains the colour of nitrophenols, which, according to the "auxochrome theory," should be less highly coloured than the corresponding ethers, the latter theory is of more general applicability.

Contrary to Hantzsch's statement that all nitrophenol ethers incapable of exhibiting tautomerism are colourless, nitroquinol dimethyl ether is yellow. In agreement with the "auxochrome theory" is the colour of sodium *m*-nitrophenoxides and the formation of yellow nitro-derivatives by hydrocarbons, such as chrysene and pyrene.



The methoxy-, acetoxy-, and acetyl-amino-groups and iodine are only weak, whilst the nitro-, amino-, and dialkyl-amino-groups are strong auxochromes. The auxochromic influence of bromine is weak and uncertain; that of chlorine is negative. G. Y.

**Nitrophenolsulphonic Acids.** ROBERT GNEHM and OSKAR KNECHT (*J. pr. Chem.*, 1906, [ii], 73, 519—537).—Whilst *o*-nitrophenol-*p*-sulphonic acid is formed by the action of fuming sulphuric acid (Kekulé, *Jahresber.*, 1867, 641) or of chlorosulphonic acid on *o*-nitrophenol (Mazurowska, this Journal, 1875, 875; 1876, ii, 61), sulphonation of *o*-nitrophenol in presence of mercury (Iljinski, Abstr., 1904, i, 176; Schmidt, *ibid.*, 256) leads to the formation of a mixture of sulphonic acids, of which *o*-nitrophenoltrisulphonic acid is isolated in the form of its barium salt,  $C_6H_3O_{12}NS_3Ba_2$ .

*o*-Nitrophenol-*p*-sulphonic acid crystallises from chloroform in glistening prisms, loses  $CHCl_3$  at 80—90°, and melts at 141—142°. The potassium salt crystallises with 1 mol. of water.

*m*-Nitrophenolsulphonic acid,  $NO_2 \cdot C_6H_3(OH) \cdot SO_3H$ , formed from *m*-nitrophenol by the action of fuming sulphuric acid, or in small yields by sulphonation in presence of mercury, crystallises in large, colourless, transparent, hexagonal leaflets containing  $4H_2O$  and melting at 50—60°; the anhydrous acid is hygroscopic, melts at 105—107°, when heated above its melting point forms a sublimate of *m*-nitrophenol, and when warmed with bromine water yields dibromo-*m*-nitrophenol (compare Willgerodt and Mohr, Abstr., 1886, 1030). The sodium,  $C_6H_3O_6NSNa_2$ , sodium hydrogen, and barium,  $C_6H_3O_6NSBa, H_2O$ , salts are described.

The *m*-aminophenolsulphonic acid, formed by reduction of the above nitro-acid is probably identical with the acid obtained by direct sulphonation of *m*-aminophenolsulphonic acid (D.R.-P. 83447) and with Klappert's electrolytic reduction product (Abstr., 1903, i, 85). The barium hydrogen salt,  $(C_6H_6O_4NS)_2Ba, 4H_2O$ , crystallises in brown needles and prisms. A comparative table of the properties of the known *m*-aminophenols is given.

*p*-Nitrophenol-*o*-sulphonic acid is obtained in a 45 per cent. yield by direct sulphonation of *p*-nitrophenol (Post, Abstr., 1881, 92). The presence of catalytic agents such as mercury, boric acid, or infusorial earth, or the use of alkali polysulphates, influences the yield, but not the constitution, of the product. *p*-Nitrophenolsulphonic acid cannot be obtained by the action of chlorosulphonic acid on *p*-nitrophenol.

G. Y.

**Reaction of an Oxydase Type exhibited by Halogen Derivatives of the Rare Earths.** EUGÈNE FOUARD (*Compt. rend.*, 1906, 142, 1163—1165).—The accelerating action of the chlorides of the metals of the rare earths on the absorption of oxygen by quinol is much greater than the corresponding action of the chlorides of the alkali and alkaline earth metals (this vol., i, 421). The experiments were conducted by placing equal volumes of equivalent solutions of the metallic chlorides together with a definite quantity of a solution of

quinol into tubes, which were then sealed and placed in an oil-bath. After eight days the volume of oxygen present in the residual air was measured, and the ratio  $R$  between the volume of oxygen absorbed and the original volume of oxygen is given in the following table:

Solution of chloride.			Ratio $R$ per cent.	
Samarium	chloride	.....	75.75	per cent.
Thorium	"	.....	63.10	"
Cerium	"	.....	57.71	"
Neodymium	"	.....	54.23	"
Praseodymium	"	.....	53.35	"
Lanthanum	"	.....	22.60	"
Sodium	"	.....	17.82	"

M. A. W.

**Cholesterol. I. Addition of Hydrogen Chloride.** JULIUS MAUTHNER (*Monatsh.*, 1906, 27, 305—314. Compare Mauthner and Suida, *Abstr.*, 1894, i, 486; 1903, i, 625; 1904, i, 49).—*Chlorocholestanol* (*cholesterol hydrochloride*),  $C_{27}H_{45}OCl$ , is formed together with  $\beta$ -dichlorocholestane by the action of hydrogen chloride on cholesterol dissolved in a mixture of ether and absolute alcohol cooled by ice; it crystallises from a mixture of chloroform and light petroleum in glistening, pliant, slender needles, melts and decomposes at  $154$ — $155^\circ$ , does not form an additive compound with bromine, and when distilled loses hydrogen chloride, forming cholesterylene. It is decomposed by concentrated sulphuric acid, but is stable towards fuming nitric acid at the ordinary temperature, and when hydrolysed with alcoholic potassium hydroxide or acetate yields cholesterol, together with an oily product, probably an isomeride.

$\beta$ -*Dichlorocholestane*,  $C_{27}H_{44}Cl_2$ , separates slowly from the ethereal-alcoholic filtrate from chlorocholestanol; it crystallises from a mixture of alcohol and benzene in flat needles, melts at  $117^\circ$ , and is stable towards fuming nitric acid, but is decomposed by concentrated sulphuric acid only slowly, forming a solution with slight green fluorescence. The  $\beta$ -dichloro-derivative is formed also by the action of hydrogen chloride on cholesteryl chloride, and is isomeric with cholestene dichloride ( $\alpha$ -dichlorocholestane), previously described (Mauthner and Suida, *Abstr.*, 1894, i, 326).

*Chlorocholestanol*,  $C_{27}H_{45}Cl$ , is formed by the action of hydrogen chloride on cholestene in chloroform solution; it crystallises in glistening, flat prisms or sheaves of iridescent leaflets, commences to sinter at  $80^\circ$ , melts at  $91^\circ$ , dissolves in boiling alcohol, and does not react with bromine in chloroform solution.

The above additive compounds of laevorotatory cholestene, cholesterol, and cholesteryl chloride are dextrorotatory. G. Y.

**Cholesterol. VI.** ADOLF WINDAUS (*Ber.*, 1906, 39, 2008—2014. Compare *Abstr.*, 1904, i, 49, 667, 1010; 1905, i, 128; this vol., i, 174; Diels and Abderhalden, this vol., i, 272).—The oxidation of cholestenone by potassium permanganate in neutral solution leads to the formation of ( $\alpha$ ) a small quantity of a *monobasic acid*,  $C_{27}H_{44}O_4$ ,

which crystallises from dilute alcohol in long, thin needles and melts at  $217-218^{\circ}$ , and (b) a *keto-acid*,  $C_{26}H_{42}O_3$ , which crystallises from a mixture of benzene and light petroleum in tetragonal leaflets and melts at  $155^{\circ}$ . The *oxime*,  $C_{26}H_{42}O_3 \cdot N \cdot OH$ , crystallises in long, thin prisms and melts and decomposes at  $191^{\circ}$ . When brominated in glacial acetic acid solution, the *keto-acid* yields the *bromo-derivative*,  $C_{26}H_{41}O_3Br$ , which crystallises in needles, melts at  $154-156^{\circ}$ , and forms a *hydroxyketo-acid* when boiled with aqueous potassium hydroxide.

Oxidation of the *keto-acid* with bromine in aqueous potassium hydroxide leads to the formation of a hygroscopic *tricarboxylic acid*,  $C_{26}H_{42}O_6$ , which crystallises from benzene in stellate groups of needles, melts at  $129-131^{\circ}$ , and decomposes when more highly heated.

The author considers that the formation of the *keto-acid* from cholestenone shows that the latter cannot be an  $\alpha\beta$ -unsaturated ketone. G. Y.

**Cholesterol. VII.** ADOLF WINDAUS (*Ber.*, 1906, 39, 2249—2262. Compare *Abstr.*, 1904, i, 49, 667, 1010; 1905, i, 128; this vol., i, 174, and preceding abstract; van Oordt, *Inaug. Diss.*, 1901, Freiburg, i/B).—When a solution of cholesterol in a mixture of benzene and glacial acetic acid is oxidised by chromic acid, one of the products is an acid,  $C_{27}H_{44}O_4$ , which melts at  $290^{\circ}$ ; its identity with the acid obtained by Diels and Abderhalden (*Abstr.*, 1904, i, 880) as a product of the oxidation of cholesterol with potassium hypobromite was further indicated by its conversion into the monomethyl ester melting at  $124^{\circ}$ .

When oxycholestenone is heated at  $180^{\circ}$  for two hours with zinc dust, it is converted into cholestandione, identical with the product which the author had previously obtained from nitrocholesterol. A comparison of the formulæ for oxycholestenone,  $C_{27}H_{40}O_2$ , and for cholestandione,  $C_{27}H_{42}O_2$ , shows that in the reduction of the former by zinc dust a hydroxy-group had not been replaced by hydrogen, as would have been the case had oxycholestenone possessed a tertiary hydroxy-group; it is probable, on the other hand, that a simple addition of two hydrogen atoms had been effected. The conversion of oxycholestenone into cholestandione may be carried out quantitatively by reducing it with zinc and acetic acid at a lower temperature than  $180^{\circ}$ . The conclusion is accordingly drawn that oxycholestenone is an unsaturated diketone.

The presence of an enolic group in oxycholestenone is indicated by the formation of an ethyl ether and a benzyl ether. The ethyl ether is readily hydrolysed.

When oxycholestenone in ethereal solution is acted on by 20 per cent. potassium hydroxide, the yellow potassium salt of oxycholestenone separates and yields the characteristic phenylhydrazone. When this salt is allowed to remain under diminished pressure for several days, it undergoes transformation into a salt of an acid and no longer yields a hydrazone. This observation also supports the view that oxycholestenone contains an enolic group.

The dibromo-derivative of cholestandione is identical with the com-



compound obtained by the addition of bromine to oxycholestenone. By the further action of bromine, each is converted into *tribromocholestandione*,  $C_{27}H_{39}O_2Br_3$ , which separates from acetone in needles and melts at  $195^\circ$ . The two bromine atoms in oxycholestenone dibromide are probably in the 1 : 2-position.

It is highly probable that the keto-groups in cholestandione and oxycholestenone respectively are in the 1 : 4-position.

The compound,  $C_{54}H_{85}O_3N(?)$ , formed by heating cholestandione with alcoholic ammonia for six hours at  $120^\circ$ , separates from a mixture of chloroform and alcohol in needles which melt and decompose at over  $300^\circ$ .

The compound,  $C_{27}H_{42}N_2$ , formed by the action of hydrazine hydrate on cholestandione, separates from a mixture of benzene and methyl alcohol in tetragonal leaflets and softens at about  $188^\circ$ . In the formation of this compound, 1 mol. of the diketone interacts with 1 mol. of hydrazine with the elimination of 2 mols. of water.

The compound,  $C_{27}H_{42}ON_2$ , formed by the action of hydrazine hydrate on oxycholestenone, crystallises in yellow leaflets and melts at  $160-161^\circ$ .

The compound,  $C_{33}H_{46}ON_2$ , formed by the action of *o*-phenylenediamine on oxycholestenone, separates from ethyl acetate in brick-red leaflets and melts at  $158-159^\circ$ .

The compound,  $C_{27}H_{42}O_6S(?)$ , formed by the action of acetic anhydride and sulphuric acid on oxycholestenone, separates from benzene in needles and decomposes at about  $148^\circ$ .

The compound,  $C_{29}H_{45}O_3N$ , prepared by the action of hydroxylamine hydrochloride and sodium acetate on  $\beta$ -oxycholestenol acetate, separates from a mixture of benzene and light petroleum in needles and melts at  $185-186^\circ$ .

In cholesterilene, there is no system of conjugated double linkings. It is not acted on by sodium and ethyl (or amyl) alcohol.

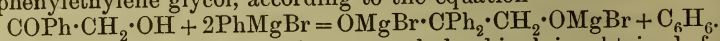
Oxycholestenone is formed when cholesterilene is oxidised by chromic acid.

A. McK.

**Synthesis of Aldehydes and Ketones from *as*-Disubstituted Ethylene Glycols and their Ethers.** RICHARD STOERMER, E. FREIHERR) SCHENCK ZU SCHWEINSBERG, FR. SIBBERN-SIBBERS, and P. RIEBEL (*Ber.*, 1906, 39, 2288-2306).—*Diphenylphenoxyethylcarbinol*,  $OH \cdot CPh_2 \cdot CH_2 \cdot OPh$ , obtained in 71 per cent. yield by the interaction of magnesium phenyl bromide and ethyl phenoxyacetate, separates from alcohol in large, rhombic crystals and melts at  $101^\circ$ . When heated with alcoholic potash for twenty hours at  $200^\circ$ , it yields two products, diphenylethoxymethylcarbinol (compare Béhal and Sommelet, *Abstr.*, 1904, i, 222), which is identical with the synthetic ether obtained from magnesium phenyl bromide and ethyl ethoxyacetate, and diphenylethyleneglycol (compare Paal and Weidenkaff, *this vol.*, i, 583), the *diacetate* of which melts at  $145.5^\circ$ . Both compounds are changed by boiling 20 per cent. sulphuric acid into diphenylacetaldehyde, the glycol completely, the ether to the extent of two-thirds. Dry diphenylethylene glycol is decomposed by

heating, yielding formaldehyde and benzhydrol, the latter being further changed into diphenylmethane and benzophenone.

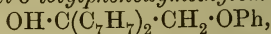
Benzoylcarbinol is conveniently obtained in good yield by digesting a cold alcoholic solution of bromoacetophenone with excess of potassium acetate; after a short heating on the water-bath, the hot liquid is poured into ice-cold water and the acetate thus obtained purified according to Fischer and Busch's directions (Abstr., 1891, 1514). Benzoylcarbinol reacts with magnesium phenyl bromide to form diphenylethylene glycol, according to the equation



In a similar way, diphenylphenoxyethylcarbinol is obtained from phenoxyacetophenone and magnesium phenyl bromide.

*Phenoxydi-p-tolyloethylene*,  $\text{C}(\text{C}_7\text{H}_7)_2 \cdot \text{CH} \cdot \text{OPh}$ , is obtained when magnesium *p*-tolyl bromide (2 mols.) reacts with ethyl phenoxyacetate (1 mol.). It crystallises in colourless needles and melts at  $122^\circ$ . When heated for twelve hours at  $240^\circ$  with alcoholic potash, it yields di-*p*-tolylethylene and ethoxydi-*p*-tolylethylene; the latter is converted by hot 20 per cent. hydrochloric acid into *di-p-tolylacetaldehyde*,  $\text{CH}(\text{C}_7\text{H}_7)_2 \cdot \text{CHO}$ , a colourless oil, which boils at  $213^\circ$  under 26 mm. pressure, reduces Fehling's and silver solutions, and forms an *oxime* crystallising in small, colourless needles and melting at  $126.5^\circ$ , and a *semicarbazone* which melts at  $185^\circ$ .

Magnesium *o*-tolyl bromide and ethyl phenoxyacetate react in the normal way, forming *di-o-tolylphenoxyethylcarbinol*,



which crystallises in colourless needles and melts at  $130^\circ$ .

*Dimethylphenoxyethylcarbinol*,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{OPh}$ , obtained like the corresponding diphenyl compound, is a colourless oil with a sweet odour, which boils at  $119^\circ$  under 16 mm. and at  $231^\circ$  under the ordinary pressure, and forms a *phenylurethane* which melts at  $70^\circ$ . When heated with alcoholic potash at  $200^\circ$ , it yields dimethylethoxymethylcarbinol (compare Béhal and Sommelet, *loc. cit.*), which is converted by 20 per cent. sulphuric acid into *isobutaldehyde*.

Phenoxyethyldiethylcarbinol,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{CEt}_2 \cdot \text{OH}$ , boils at  $259$ — $260^\circ$  and forms a *phenylurethane* which melts at  $98^\circ$ . Ethoxyethyldiethylcarbinol yields diethylacetaldehyde by boiling with 20 per cent. sulphuric acid.

*$\beta$ -Phenylpropylene  $\alpha\beta$ -glycol*,  $\text{OH} \cdot \text{CMePh} \cdot \text{CH}_2 \cdot \text{OH}$ , to the extent of 7.5, and its *anhydride*,  $\text{CMePh} \left\langle \begin{smallmatrix} \text{CH}_2 \cdot \text{O} \\ \text{O} \cdot \text{CH}_2 \end{smallmatrix} \right\rangle \text{CMePh}$ , to the extent of 25 per cent., are obtained by the interaction of magnesium methyl iodide and benzoylcarbinol; they are separated by water, in which the former is easily soluble. The glycol forms colourless needles, melts at  $44.5^\circ$ , boils at  $158$ — $160^\circ$  under 25 mm. pressure, and is partially changed into hydratropaldehyde by 20 per cent. sulphuric acid. The anhydride, which is a yellow, odourless oil boiling at  $194^\circ$  under 15 mm. pressure, is not identical with Klages' oxide (Abstr., 1905, i, 523); it is converted by slightly acidified water at  $180^\circ$  into hydratropaldehyde.

*$\beta$ -Phenylbutylene  $\alpha\beta$ -glycol*,  $\text{OH} \cdot \text{CEtPh} \cdot \text{CH}_2 \cdot \text{OH}$ , and its *anhydride*,  $\text{C}_{20}\text{H}_{24}\text{O}_2$ , are obtained from an ethereal solution of magnesium ethyl

iodide and benzoylcarbinol suspended in dry benzene, the relative yields depending on the order in which the one solution is added to the other. The former compound crystallises in needles, melts at  $56^{\circ}$ , and boils at  $158\text{--}161^{\circ}$  under 20 mm. pressure; the latter is a viscous, yellow oil, which boils at  $221\text{--}223^{\circ}$  under 20 mm. pressure, and is difficultly volatile in steam.

*α-Phenylbutaldehyde*,  $\text{CHEtPh}\cdot\text{CHO}$ , obtained from the preceding reaction products by slightly acidified water at  $180^{\circ}$ , is a colourless oil with a strong agreeable odour, which boils at  $104\text{--}106^{\circ}$  under 15 mm. and at  $211^{\circ}$  under the ordinary pressure; the *oxime* is an oil, but the *semicarbazone*, best obtained from the sodium hydrogen sulphite compound, melts at  $155^{\circ}$ .

By the action of magnesium phenyl bromide on ethyl *α*-phenoxypropionate, the *phenyl ether* of *ββ*-diphenylpropylene-*αβ*-glycol,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CHMe}\cdot\text{OPh}$ , is obtained, which melts at  $136^{\circ}$ . Alcoholic potash at  $220^{\circ}$  converts it into an oil, from which *ββ*-diphenylpropylene

*oxide*,  $\text{O} < \begin{array}{c} \text{CHMe} \\ | \\ \text{CPh}_2 \end{array}$ , was isolated, but not the corresponding ethyl

ether in the pure state; the former melts at  $67^{\circ}$ , boils above  $300^{\circ}$  with slight decomposition, and forms an oily *chlorohydrin*,  $\text{C}_{15}\text{H}_{15}\text{OCl}$ .

*αα*-Diphenylpropylene *αβ*-glycol,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CHMe}\cdot\text{OH}$ , obtained from ethyl lactate by the Grignard method, crystallises in long needles and melts at  $96.5^{\circ}$ ; the *diacetate* melts at  $153^{\circ}$ .

*Diphenylacetone*,  $\text{CHPh}_2\cdot\text{COMe}$ , obtained quantitatively from the preceding glycol and slightly acidified water at  $180^{\circ}$ , is dimorphous, the one form melting at  $46^{\circ}$ , the other at  $61^{\circ}$ . The less fusible substance has not been transformed into its isomeride, but both yield the same *oxime*, which melts at  $164.5^{\circ}$ , *semicarbazone*, which melts at  $170^{\circ}$ , and *phenylhydrazone*, which melts at  $131^{\circ}$ .

*ββ*-Di-*p*-tolylpropylene *αβ*-glycol,  $\text{OH}\cdot\text{C}(\text{C}_7\text{H}_7)_2\cdot\text{CHMe}\cdot\text{OH}$ , prepared in similar manner, melts at  $67^{\circ}$ , and when heated with acetic anhydride forms *di-p-tolylacetone*,  $\text{CH}(\text{C}_7\text{H}_7)_2\cdot\text{COMe}$ , which is also obtained by the direct distillation of the glycol; it boils at  $194^{\circ}$  under 20 mm. pressure. The *oxime* melts at  $189^{\circ}$ , the *semicarbazone* at  $172^{\circ}$ , and the *phenylhydrazone* at  $122^{\circ}$ . Di-*o*-tolylpropylene glycol is not obtained from magnesium *o*-tolyl bromide and ethyl lactate; when the reaction product is decomposed by ice and acetic acid, an oil is obtained from which a substance, apparently *o-tolualdehyde*, is obtained, together with *di-o-tolylacetone*,  $\text{CH}(\text{C}_7\text{H}_7)_2\cdot\text{COMe}$ , which is a viscous oil, boils at  $198^{\circ}$  under 12 mm. pressure, and does not form a sodium hydrogen sulphite compound. The *oxime* melts at  $171^{\circ}$ , the *semicarbazone* at  $152^{\circ}$ .

C. S.

**Unsymmetrical Diphenylethylene Oxide and Diphenylethylene Glycol.** CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1906, 39, 2062—2063. Compare *Abstr.*, 1905, i, 436; this vol., i, 236).—*as*-Diphenylethylene oxide (Klages and Kessler, this vol., i, 498) may be obtained by the action of nitrous acid on diphenylaminomethylcarbinol. *as*-Diphenylethylene glycol,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{OH}$ , is readily prepared by the action of magnesium phenyl bromide on ethyl glycolate.



It crystallises from its aqueous solution in large, colourless needles, melting at  $121^{\circ}$ , and dissolves readily in most organic solvents.

J. J. S.

**Optically Active 4-Methylcyclohexylidene-1-acetic Acid.** WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, 39, 2035—2038. Compare this vol., i, 360; Perkin and Pope, *Proc.*, 1906, 22, 107).—The acid previously described readily loses carbon dioxide, yielding a hydrocarbon,  $C_8H_4$ , already described by Wallach, and its products of oxidation prove it to be 1-methyl-4-methylenecyclohexane. The constitution of the acid is therefore regarded as established.

The cinchonine salt, when pure, melts at  $62-64^{\circ}$ , and has  $[\alpha]_D + 16.0^{\circ}$ .

J. J. S.

**Simple Method for the Synthesis of  $\alpha$ -Amino-acids.** HANS BUCHERER (*Ber.*, 1906, 39, 2033—2034).—Priority as against Zelinsky and Stadnikoff (this vol., i, 425) is claimed (compare *Abstr.*, 1905, i, 438).

J. J. S.

**Phenylbutyric Acids and their  $\alpha$ -Amino-derivatives.** EMIL FISCHER and WILHELM SCHMITZ (*Ber.*, 1906, 39, 2208—2215. Compare this vol., i, 182; Knoop and Hössli, *ibid.*, 431).—Chloroethylbenzene prepared by the action of chlorine on boiling ethylbenzene consists principally of the  $\alpha$ -isomeride, as when boiled with copper nitrate solution it is oxidised to acetophenone, which is obtained in a yield of more than 60 per cent. of the theoretical. The following constitutions must therefore be ascribed to the derivatives of malonic and phenylbutyric acids previously described: *ethyl  $\beta$ -phenylethylmalonate*,  $CHMePh \cdot CH(CO_2Et)_2$ , instead of *ethyl  $\gamma$ -phenylethylmalonate*;  *$\beta$ -phenylethylmalonic acid*,  $CHMePh \cdot CH(CO_2H)_2$ , instead of  *$\gamma$ -phenylethylmalonic acid*;  *$\alpha$ -bromo- $\beta$ -phenylethylmalonic acid*,  $CHMePh \cdot CBr(CO_2H)_2$ ,

instead of  *$\alpha$ -bromo- $\gamma$ -phenylethylmalonic acid*; and  *$\alpha$ -bromo- $\beta$ -phenylbutyric acid*,  $CHMePh \cdot CHBr \cdot CO_2H$ , and  *$\alpha$ -amino- $\beta$ -phenylbutyric acid*,  $CHMePh \cdot CH(NH_2) \cdot CO_2H$ , instead of  *$\alpha$ -bromo- and  $\alpha$ -amino- $\gamma$ -phenylbutyric acids* respectively. The terms *prim.*-phenethyl and *sec.*-phenethyl are used by the authors for the groups  $CHPh \cdot CH_2$  and  $CHMePh$  respectively.

The following derivatives of  $\gamma$ -phenylethylmalonic and  $\gamma$ -phenylethylbutyric acids have been prepared from Grignard's  $\omega$ -bromoethylbenzene (*Abstr.*, 1904, i, 213) in the same way as the  $\beta$ -phenyl compounds from  $\alpha$ -chloroethylbenzene.

*Ethyl  $\gamma$ -phenylethylmalonate*,  $CH_2Ph \cdot CH_2 \cdot CH(CO_2Et)_2$ , is obtained as a colourless, viscid oil, which boils at  $178-182^{\circ}$  under 16 mm. pressure. The *acid*,  $CH_2Ph \cdot CH_2 \cdot CH(CO_2H)_2$ , crystallises from benzene in microscopic needles, or from hot water in sheaves of small, colourless, pointed needles, melts and evolves carbon dioxide at  $130-131^{\circ}$  (corr.), and when heated at  $140^{\circ}$  yields  $\gamma$ -phenylbutyric acid.

*$\alpha$ -Bromo- $\gamma$ -phenylethylmalonic acid*,  $CH_2Ph \cdot CH_2 \cdot CBr(CO_2H)_2$ , crystallises from water in slender needles, melts and decomposes at  $158^{\circ}$

(corr.), and when heated at 160—165° yields *α*-bromo-*γ*-phenylbutyric acid, which is obtained as a viscid oil.

*α*-Amino-*γ*-phenylbutyric acid, prepared from the preceding bromo-acid, is identical with Knoop and Hössli's acid (*loc. cit.*). The copper salt forms a slightly blue, flocculent precipitate, which is only sparingly soluble in water.

*β*-Phenylbutyric acid,  $\text{CHMePh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , formed by heating *β*-phenylethylmalonic acid above its melting point, crystallises from water in small needles, or from light petroleum in small prisms, melts at 38—39° (corr.), and distils at 160° under 16 mm. or at 270° under the ordinary pressure. It forms a calcium salt, which separates from its aqueous solution when heated as a viscid oil, redissolving as the solution cools. The lead salt forms a white, amorphous precipitate; the silver salt,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Ag}$ , forms slender needles. G. Y.

**Stereoisomeric Cinnamic Acids.** WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, 39, 1966. Compare this vol., i, 360).—A reply to Erlenmeyer, jun., and Barkow (this vol., i, 429).

G. Y.

**Derivatives of *o*-Nitromandelonitrile.** GUSTAV HELLER and HEINRICH G. MAYER (*Ber.*, 1906, 39, 2334—2339).—*o*-Nitromandelonitrile forms an *acetyl* derivative which melts at 52° and a *benzoyl* derivative which melts at 90—91°; the *amide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OBz}) \cdot \text{CO} \cdot \text{NH}_2$ , of the latter melts at 128°. *Ethyl o-nitrobenzoylmandelate*,  
 $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OBz}) \cdot \text{CO}_2\text{Et}$ ,

melts at 72°.

Benzoyldioxindole is obtained by reducing ethyl *o*-nitrobenzoylmandelate or the amide with stannous chloride and hydrochloric acid, and is identical with the substance obtained by benzoylating dioxindole (*Abstr.*, 1904, i, 416).

*o*-Nitrosobenzoic acid is the chief product formed when *o*-nitromandelonitrile is dissolved in alcoholic ammonia (compare *Ber.*, 1901, 34, 948); the *methyl* ester, obtained by the use of methyl sulphate and sodium carbonate, melts at 152—153°, and when reduced yields methyl anthranilate. C. S.

**A New Step in the Reduction of the Nitro-group.** GUSTAV HELLER (*Ber.*, 1906, 39, 2339—2346).—The first step in the reduction of the nitro-group is the formation of the group  $\text{N}(\text{OH})_2$ . When *o*-nitromandelonitrile, dissolved in 33 per cent. acetic acid, is cooled to 0° and treated with zinc dust, a *substance* is obtained which crystallises in quadratic plates or leaflets, decomposes at 145°, and reduces solutions of gold, silver, and platinum salts. From its composition and behaviour, the substance is regarded as a quinhydrone-like compound, composed of  $\text{N}(\text{OH})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CN}, \text{HCl}$  and  
 $\text{OH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CN}, \text{HCl}$ .

When heated on the water-bath with water and hydrochloric acid, about 40 per cent. of the substance is changed into *o*-nitrosomandelonitrile,  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CN}$ , which crystallises in colourless needles with a faint blue shade, melts at 210°, and is converted by boiling dilute alkali hydroxides into anthroxanic acid. When warmed with ferrous sulphate and sodium hydroxide and then acidified, the substance

yields isatin, but if ammonia and ferrous sulphate are used, followed by sodium hydroxide, and the solution is then acidified and concentrated, isatyde is obtained.

When the quinhydrone compound is warmed with hydrochloric acid, the second of the components mentioned above yields isatin.

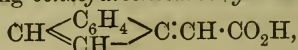
By acetylation, the substance yields isatin and 1-acetoxyisatin,  $C_6H_4 \begin{smallmatrix} \text{N(OAc)} \\ \text{CO} \end{smallmatrix} \text{CO}$ , which separates from benzene in orange-red plates, melts at 151–152°, gives the indophenin reaction, and by solution in an alkali hydroxide, followed by the addition of excess of hydrochloric acid, yields anthroxanic acid.

When 1-acetoxyisatin is treated with alcohol and phenylhydrazine, yellowish-green leaflets of 1-hydroxyisatinphenylhydrazone,  $C_{14}H_{11}O_2N_3$ , are obtained, which melt at 220°, but when it is warmed with excess of alcohol and phenylhydrazine, the osazone,  $C_{20}H_{17}ON_5$ , is formed, which crystallises in slender, yellow needles and melts at 169°. C. S.

**Derivatives of Fulvene. II. Derivatives of Indeneoxalic Esters.** JOHANNES THIELE and MAX RÜDIGER (*Annalen*, 1906, 347, 275–289. Compare this vol., i, 569; Thiele, *Abstr.*, 1900, i, 347; Wislicenus, *ibid.*, 346).—In accordance with the strong colour of indeneoxalic esters, these are represented as the enolic form, in which they are derivatives of the strongly coloured fulvene.

*Methyl indeneoxalate*,  $CH \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} C:C(OH) \cdot CO_2Me$ , formed with slight development of heat by the condensation of indene and methyl oxalate in presence of sodium ethoxide in absolute alcoholic solution, crystallises from benzene in orange-red needles and melts at about 90–92°, or at lower temperatures after repeated recrystallisation.

*Ethyl α-hydroxyindeneacetate*,  $CH \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} CH \cdot CH(OH) \cdot CO_2Et$ , prepared by reduction of ethyl indeneoxalate by means of aluminium amalgam and moist ether, is obtained as a yellow, viscid oil, which boils at 172° under 13 mm. pressure, and gives a deep red coloration with much concentrated sulphuric acid. It is readily hydrolysed by methyl-alcoholic or concentrated aqueous potassium hydrobromide, losing  $H_2O$  and forming *benzofulvenecarboxylic acid*,



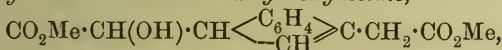
which crystallises from benzene in microscopic, orange leaflets, commences to sinter at 175°, and when more highly heated partially sublimes and finally decomposes. With alcoholic potassium hydroxide, it gives a violet-red coloration, becoming green and then yellow on addition of water, and yields methylindene when distilled with soda-lime, or in a vacuum, or in a current of hydrogen. The *methyl ester*,  $C_{12}H_{10}O_2$ , crystallises in yellow needles, melts at 62–63°, and resembles quinone in appearance.

*Indeneacetic acid*,  $CH_2 \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} C \cdot CH_2 \cdot CO_2H$ , prepared by reduction of benzofulvenecarboxylic acid by means of aluminium amalgam, or zinc dust and ammonia, or of methyl benzofulvenecarboxylate by means



of aluminium amalgam, crystallises in white needles, melts at 95—96°, remains unchanged when heated with 20 per cent. potassium hydroxide at 120° in a sealed tube, and yields methylindene when distilled with soda-lime. The *methyl* ester,  $C_{12}H_{12}O_2$ , is obtained as a yellow, viscid oil, which boils at 148—150° under 12 mm. pressure and solidifies partially when cooled by ice.

1-Oxaloindene-3-acetic acid,  $CO_2H \cdot C(OH) : C \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C \cdot CH_2 \cdot CO_2H$ , formed by hydrolysis of its esters, crystallises from dilute alcohol or acetic acid in orange-red needles, melts and decomposes at about 200°, and gives a brown to green coloration with ferric chloride. The *methyl hydrogen* ester,  $CO_2Me \cdot C(OH) : C \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C \cdot CH_2 \cdot CO_2H$ , prepared by the action of methyl oxalate on indeneacetic acid in presence of sodium methoxide in methyl-alcoholic solution, crystallises from chloroform in small, orange needles, or from a mixture of alcohol and chloroform in glistening leaflets, melts and decomposes at about 190°, and gives a transient, reddish-brown coloration with ferric chloride. The *dimethyl* ester,  $C_{15}H_{14}O_5$ , formed in the same manner from methyl indeneacetate and methyl oxalate, crystallises in yellow needles, melts at 109—110°, and gives with ferric chloride a similar coloration to the methyl hydrogen ester. When reduced with aluminium amalgam, it yields *dimethyl indene-1-acetate-3- $\alpha$ -hydroxyacetate*,

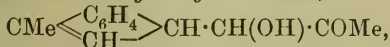


which is obtained as a yellow, viscid oil, giving a violet-red coloration with alcoholic potassium hydroxide.

*Carboxybenzofulveneacetic acid*,  $CO_2H \cdot CH_2 \cdot C \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C : CH \cdot CO_2H$ , is formed by hydrolysis of the preceding ester by means of alcoholic potassium hydroxide; it crystallises from toluene in small, light yellow needles, melts and decomposes at 240—250°, and is reduced by zinc dust and ammonia, forming a colourless acid (*indenediacetic acid*?).

1-Methylindene-3-oxalic acid,  $CMe \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > C : C(OH) \cdot CO_2H$ , is obtained by hydrolysis of its ester; it crystallises in slender, yellow needles, darkens and decomposes at about 200°, and gives a reddish-brown to green coloration with alcoholic ferric chloride, becoming colourless on addition of water. The *ethyl* ester,  $C_{14}H_{14}O_3$ , prepared from methylindene and ethyl oxalate, crystallises in orange-red needles, melts at about 92—94°, decomposes slowly at the ordinary temperature, and couples with diazobenzenesulphonic acid in acid or alkaline solution. The *methyl* ester, formed from methyl oxalate and methylindene, crystallises in hard, orange needles, melts at 135—136°, gives a transient, brown coloration with ferric chloride, and couples with diazobenzenesulphonic acid.

*Methyl 1-methylindene-3- $\alpha$ -hydroxyacetic acid*,



formed by reduction of methyl methylindeneoxalate, is obtained as a

yellow, viscid oil, which decomposes when distilled, and gives with alcoholic potassium hydroxide a cherry-red, with concentrated sulphuric acid a red solution with green fluorescence.

1-Methylbenzofulvenecarboxylic acid,  $\text{CMe} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C}:\text{CH}\cdot\text{CO}_2\text{H}$ , prepared in the same way as benzofulvenecarboxylic acid, crystallises from benzene in orange needles and decomposes above  $200^\circ$ .

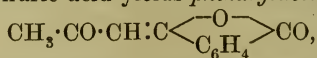
1-Methylindene-2-carboxylic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CMe} \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{H}$  (Roser, Abstr., 1888, 1303), forms a *methyl* ester,  $\text{C}_{12}\text{H}_{12}\text{O}_2$ , which crystallises in white needles and melts at  $78^\circ$ , and an *ethyl* ester,  $\text{C}_{13}\text{H}_{14}\text{O}_2$ , which forms needles and melts at  $38^\circ$ .  
G. Y.

**Gabriel's Conversion of Phthalides into Indanediones.** ALEXANDER FIBNER (*Ber.*, 1906, 39, 2202—2204. Compare Nathanson, Abstr., 1894, i, 37).—Quinolylacetophenone-*o*-carboxylic acid is converted into the red sodium derivative of quinophthalone by sodium ethoxide, not directly, but if first heated with alcohol and a small quantity of concentrated hydrochloric or sulphuric acid. The reaction takes place therefore between sodium ethoxide and *ethyl quinolylacetophenone-o-carboxylate*,  $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}$ . This crystallises from light petroleum in yellow needles and melts at  $250^\circ$ .

The conversion of *as*-quinophthalone into its sodium derivative by the action of alcoholic sodium ethoxide takes place in two stages: the first is marked by the formation of a golden-yellow solution; the second, in which the red colour of the sodium derivative appears, takes place slowly at the ordinary temperature, but quickly on heating. The intermediate product is probably the above ester or its sodium derivative.  
G. Y.

**Transformations of Phthalylacetylacetone.** CARL BÜLOW and MAX DESENISS (*Ber.*, 1906, 39, 2275—2281. Compare Abstr., 1904, i, 610; 1905, i, 42, 529).—Phthalylacetylacetone is decomposed into acetylacetone and phthalic acid by boiling water; into phthalamide and phthalimide by alcoholic ammonia, and into methylphthalimide by 30 per cent. methylamine at  $100^\circ$ . A solution of sodium hydroxide in the cold, of sodium carbonate or hydrogen carbonate when warmed, and of barium hydroxide when boiled, decomposes phthalylacetylacetone into phthalic acid and acetylacetone.

The reaction between phthalylacetylacetone and ten times its weight of concentrated sulphuric acid yields *phthalylacetone*,



which separates from alcohol in white, feathery crystals and melts at  $183^\circ$ .

Phthalylacetylacetone is transformed by sodium methoxide into 2-acetyl-1:3-diketohydrindene, and is decomposed by hydrazine yielding  $\beta$ -phthalylhydrazine; by semicarbazine yielding *phthalylsemicarbazide*,  $\text{C}_9\text{H}_7\text{O}_3\text{N}_3$ , which melts at  $249^\circ$ ; by *p*-nitrophenylhydrazine yielding *phthalyl-p-nitrophenylhydrazide*,  $\text{C}_{14}\text{H}_9\text{O}_4\text{N}_3$ , which melts at

247°. With hydroxylamine, the substance reacts normally, yielding *phthalylacetylacetone monoxime*,  $C_{13}H_{11}O_4N$ , which melts at 169°.

C. S.

**Syntheses of Aromatic Aldehydes. I. LUDWIG GATTERMANN** (*Annalen*, 1906, 347, 347—386. Compare Gattermann and Koch, Abstr., 1897, i, 519; Gattermann and Frenzel, Abstr., 1898, i, 476; Gattermann and Berchemann, *ibid.*, 581; Gattermann and Köbner, Abstr., 1899, i, 363; Gattermann and Maffezzoli, Abstr., 1904, i, 172).—The aldehydes described in this paper, which opens with a *résumé* of the author's three methods for the synthesis of aromatic aldehydes, have been prepared by the action of carbon monoxide and hydrogen chloride on hydrocarbons in presence of aluminium chloride and cuprous chloride.

Benzaldehyde is formed from benzene by this method only if aluminium bromide is substituted for the chloride. Dibenzylidenebenzidine melts at 234°, forming a liquid crystalline phase, changing to a clear liquid at 260°. The condensation products of other aromatic aldehydes with benzidine and substituted benzidines behave in the same manner.

When heated with concentrated hydriodic acid and red phosphorus in a sealed tube, *p*-tolualdehyde is reduced to *p*-xylene. Di-*p*-toluylidenebenzidine melts at 230°, forming a turbid liquid which becomes clear above the boiling point of sulphuric acid. Tolylideneazine melts at 158°; the phenylhydrazone melts at 112—113°. When reduced electrolytically in a mixture of glacial acetic acid and concentrated sulphuric acid with an *E.M.F.* of 5—6 volts and a current density of 1.2 amperes, *m*-nitro-*p*-tolualdehyde, which melts at 48—49° (43—44°, Hanzlik and Bianchi, Abstr., 1899, i, 597), yields the

compound  $COH \cdot C_6H_3Me \cdot N < \overset{O}{\underset{||}{CH}} \cdot C_6H_3Me \cdot NO_2$ . This separates from benzene in yellow crystals, melts at 168°, and when oxidised with ferric chloride forms *nitroso-p-tolualdehyde*,  $C_8H_7O_2N$ , which crystallises in glistening, silvery needles and melts at 128°. 2:6-Dinitro-*p*-tolualdehyde,  $C_6H_2Me(NO_2)_2 \cdot COH$ , formed by the action of a mixture of fuming nitric and concentrated sulphuric acids on *p*-tolualdehyde, crystallises in yellow needles, melts at 109°, and forms 2:6-dinitro-*p*-toluic acid when oxidised with potassium permanganate.

3:5-Dinitro-4-methylbenzylidene chloride,  $C_8H_6O_4N_2Cl_2$ , formed by nitration of 4-methylbenzylidene chloride, crystallises in large, colourless needles, melts at 90°, and when hydrolysed by means of a mixture of fuming and concentrated sulphuric acids yields 2:6-dinitro-*p*-tolualdehyde.

Ethyl *p*-methylcinnamate,  $C_{12}H_{14}O_2$ , prepared by the action of ethyl acetate and sodium on *p*-tolualdehyde, is obtained as a colourless, strongly refracting oil, which boils at 278°, has an odour resembling that of ethyl cinnamate, and on hydrolysis yields *p*-methylcinnamic acid. The ester reacts with bromine in carbon disulphide solution, forming ethyl  $\alpha\beta$ -dibromo-4-methyldihydrocinnamate,  $C_{12}H_{14}O_2Br_2$ , which crystallises from alcohol in large, glistening prisms and melts at 76.5°, together with an oil, probably a stereoisomeride.  $\alpha\beta$ -Dibromo-



4-methylcinnamic acid melts at  $192^{\circ}$  ( $183^{\circ}$ , Kröber, Abstr., 1890, 968). On treatment with potassium hydroxide in hot concentrated alcoholic solution, the preceding ester yields *bromo-4-methylcinnamic acid*,  $C_{10}H_9O_2Br$ , which crystallises from benzene in white needles and melts at  $192^{\circ}$ . If in the preparation of this acid the filtrate from the potassium bromide is boiled in a reflux apparatus, the product is *p-tolylpropionic acid*,  $C_{10}H_8O_2$ , which crystallises in long, colourless prisms, melts and decomposes at  $148^{\circ}$ , and when heated with aniline loses carbon dioxide, forming *p-tolylacetylene*.

*m*-Nitro-*p*-methylcinnamic acid melts at  $173.5^{\circ}$  ( $170$ — $171^{\circ}$ , Hanzlik and Bianchi, Abstr., 1899, i, 890).

*p*-Tolylideneacetone (Hanzlik and Bianchi, *loc. cit.*) distils at  $142$ — $145^{\circ}$  under 15 mm. pressure as a strongly refracting oil. The *oxime*,  $C_{11}H_{13}ON$ , crystallises in colourless leaflets and melts at  $126^{\circ}$ . The *semicarbazone*,  $C_{12}H_{15}ON_3$ , forms colourless needles, becomes yellow on exposure to air, and melts at  $202^{\circ}$ . The *azine*,  $C_{22}H_{24}N_2$ , crystallises in yellow needles and melts at  $190^{\circ}$ . The phenylhydrazone forms yellow needles and melts at  $154^{\circ}$  ( $138^{\circ}$ , Hanzlik and Bianchi, *loc. cit.*), and when heated above its melting point changes suddenly into *phenyl-p-tolylmethylpyrazoline*,  $C_{17}H_{18}N_2$ , which crystallises from light petroleum in colourless needles, melts at  $112^{\circ}$ , forms solutions with blue fluorescence, and gives Knorr's pyrazoline reaction. *m*-Nitro-*p*-tolylideneacetone is formed by nitration of *p*-tolylideneacetone.

*Di-p-tolylideneacetone*,  $CO(CH:CH \cdot C_7H_7)_2$ , is prepared by condensation of *p*-tolylideneacetone with *p*-tolualdehyde; it crystallises from alcohol in glistening, slightly yellow needles, melts at  $175^{\circ}$ , with 2 mols. of hydrogen chloride in ethereal solution forms an unstable scarlet *hydrochloride*, and yields an *additive* compound with ferric chloride and hydrogen chloride.

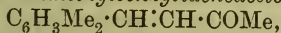
*Di-p-methylbenzoin* (Stierlin, Abstr., 1889, 513) crystallises in triclinic prisms [ $a:b:c = 0.593:1:0.282$ ;  $\alpha = 126^{\circ}51'44''$ ;  $\beta = 116^{\circ}45'2''$ ;  $\gamma = 76^{\circ}0'8''$ ].

*Di-p-methylbenzilic acid*,  $C_{16}H_{16}O_3$ , prepared by the action of aqueous potassium hydroxide on *di-p-methylbenzil*, crystallises in colourless needles, melts at  $131^{\circ}$ , and when heated at  $150^{\circ}$  forms an *anhydride*,  $C_{32}H_{30}O_5$ , which crystallises in colourless prisms and melts at  $164^{\circ}$ .

*Hydro-p-toluamide*,  $N_2(CH \cdot C_7H_7)_3$ , formed by the action of ammonia on *p*-tolualdehyde in cooled absolute alcoholic solution, crystallises in white needles, melts at  $92^{\circ}$ , and when heated at  $130$ — $140^{\circ}$  for three to four hours, dissolved in alcohol, and treated with concentrated hydrochloric acid, is converted into *tri-p-methyl-amarine*,  $C_{24}H_{24}N_2$ . This crystallises from dilute acetone in colourless needles, melts at  $127^{\circ}$ , dissolves in alcohol, forming an alkaline solution, and becomes luminescent when heated with alcoholic potassium hydroxide at  $70$ — $75^{\circ}$  in the dark. The *hydrochloride*,  $C_{24}H_{25}N_2Cl$ , crystallises in colourless needles and melts at about  $295^{\circ}$ . The *silver* derivative,  $C_{24}H_{23}N_2Ag$ , is formed as a white, amorphous precipitate. The *nitroso*-derivative,  $C_{24}H_{23}ON_3$ , forms yellow crystals and melts at  $147^{\circ}$ . When heated, *hydro-p-toluamide* yields ammonia, a polymericide of tolunitrile which melts above  $260^{\circ}$ , and trimethyl-lophine,

$C_{24}H_{22}N_2$ . This crystallises from dilute alcohol in stout needles, melts at  $234^\circ$ , is a feeble base, and is more strongly luminescent than trimethylamine when heated with alcoholic potassium hydroxide at  $70^\circ$ . The *acetate* crystallises in large octahedra, melts at  $97^\circ$ , and is decomposed by boiling alcohol.

3:4-Dimethylbenzaldehyde,  $C_9H_{10}O$ , formed from *o*-xylene, boils at  $225^\circ$ , and on oxidation yields 3:4-dimethylbenzoic acid. The *oxime*,  $C_9H_{10}NOH$ , crystallises from light petroleum in colourless needles and melts at  $69^\circ$ . The *azine*,  $N_2(C_9H_{10})_2$ , separates from alcohol in sulphur-yellow leaflets and melts at  $132^\circ$ . The *phenylhydrazone*,  $C_{15}H_{16}N_2$ , forms colourless, unstable crystals and melts at  $96^\circ$ . The *condensation* product with benzidine,  $C_{30}H_{28}N_2$ , crystallises in golden-yellow leaflets and melts at  $158^\circ$  to a turbid, at  $250^\circ$  to a clear, liquid. The *trithioaldehyde*,  $C_{27}H_{30}S_3$ , forms colourless crystals and melts at  $147^\circ$ . 3:4-Dimethylmandelic acid,  $C_{10}H_{12}O_3$ , crystallises in glistening, colourless leaflets and melts at  $105^\circ$ . 3:4-Dimethylcinnamic acid,  $C_{11}H_{12}O_2$ , is formed by acting with malonic acid on 3:4-dimethylbenzylideneaniline, and heating the product with hydrochloric acid; it crystallises in colourless needles and melts at  $142^\circ$ . The *ethyl ester*,  $C_{13}H_{16}O_2$ , formed by the action of ethyl acetate and sodium on 3:4-dimethylbenzaldehyde, is obtained as a colourless, strongly refracting, pleasant-smelling oil which boils at  $180\text{--}185^\circ$  under 22 mm. pressure. 3:4-Dimethylbenzylideneacetone,



formed in the same way as tolylideneacetone, separates from ether in stout crystals, melts at  $40^\circ$ , and boils at  $172^\circ$  under 20 mm. pressure. The *semicarbazone*,  $C_{13}H_{17}ON_3$ , crystallises in colourless needles and melts at  $207^\circ$ .

2:4-Dimethylbenzaldehyde, formed from *m*-xylene, boils at  $216\text{--}218^\circ$  (compare Bouveault, Abstr., 1896, i, 649). The *oxime*,  $C_9H_{11}ON$ , crystallises in strongly refracting prisms and melts at  $88^\circ$ . The *phenylhydrazone*,  $C_{15}H_{16}N_2$ , forms colourless leaflets and melts at  $88^\circ$ .

5-Nitro-2:4-dimethylbenzaldehyde,  $C_9H_9O_3N$ , forms yellow needles, melts at  $81^\circ$ , and on oxidation yields 5-nitro-2:4-dimethylbenzoic acid. 2:4-Dimethylmandelic acid,  $C_{10}H_{12}O_3$ , crystallises from benzene in colourless needles and melts at  $119^\circ$ . 2:4-Dimethylcinnamic acid,  $C_{11}H_{12}O_2$ , formed by the action of malonic acid and alcoholic ammonia on the aldehyde, crystallises in glistening, colourless needles and melts at  $181^\circ$ . When reduced with sodium amalgam it yields 2:4-dimethyldihydrocinnamic acid,  $C_{11}H_{14}O_2$ , which crystallises in glistening, colourless leaflets and melts at  $108^\circ$ . 2:4-Dimethylbenzylideneacetone,  $C_{12}H_{14}O$ , forms yellow crystals, melts at  $32^\circ$ , and boils at  $145\text{--}148^\circ$  under 10 mm. pressure. The *semicarbazone*,  $C_{13}H_{17}ON_3$ , crystallises from alcohol in white needles and melts at  $227^\circ$ .

*p*-Xylene does not form an aldehyde, whilst 2:4:6-trimethylbenzaldehyde is formed from mesitylene in only small quantities by the carbon monoxide method.

2:4:5-Trimethylbenzaldehyde, formed from  $\psi$ -cumene, boils at  $243^\circ$ , is oxidised by potassium permanganate in dilute alkaline solution, forming durylic acid, and is reduced to durene by hydriodic acid and

red phosphorus. When exposed to direct sunlight, the colourless crystals of the aldehyde become yellow, changing again in the dark to the colourless state (compare Marckwald, Abstr., 1900, ii, 2). The *oxime*,  $C_{10}H_{13}ON$ , crystallises from light petroleum in colourless needles and melts at  $102^{\circ}$ . The *phenylhydrazone*,  $C_{16}H_{18}N_2$ , forms colourless leaflets and melts at  $138^{\circ}$ .

The nitration of  $\psi$ -cumylaldehyde, as also that of  $p$ -xylylaldehyde and of the corresponding acetophenones, leads to the formation of the *o*-nitro-derivatives as the main products, whilst the *m*-nitro-derivatives are formed at the same time in smaller amount.

*o*-Nitro- $\psi$ -cumylaldehyde,  $C_{10}H_{11}O_3N$ , formed best at  $-5^{\circ}$  to  $-10^{\circ}$ , crystallises in almost colourless leaflets, melts at  $142^{\circ}$ , and yields hexamethylindigotin when heated gently with acetone and alcoholic potassium hydroxide. When reduced, it forms *o*-amino- $\psi$ -cumylaldehyde,  $C_{10}H_{13}ON$ , which crystallises in yellowish-green leaflets, melts at  $102$ – $103^{\circ}$ , and is volatile in a current of steam. When diazotised and boiled with dilute sulphuric acid, this yields *o*-hydroxy- $\psi$ -cumylaldehyde,  $C_{10}H_{12}O_2$ , which crystallises from alcohol in colourless leaflets and melts at  $78$ – $79^{\circ}$ .

*o*-Nitrodurylic acid,  $C_{10}H_{11}O_4N$ , formed by oxidation of the *o*-nitro-aldehyde with potassium permanganate, crystallises in colourless needles and melts at  $192$ – $193^{\circ}$ . *6*-Nitro-2:4:5-trimethylcinnamic acid,  $C_{12}H_{13}O_4N$ , formed by the action of sodium acetate and acetic anhydride on the *o*-nitro-aldehyde, crystallises from alcohol in slightly yellow leaflets and melts at  $186$ – $187^{\circ}$ .

*m*-Nitro- $\psi$ -cumylaldehyde,  $C_{10}H_{11}O_3N$ , crystallises from alcohol in long, colourless needles and melts at  $128^{\circ}$ . *Dinitro- $\psi$ -cumylaldehyde*,  $C_{10}H_{10}O_5N_2$ , prepared by the action of potassium nitrate and concentrated sulphuric acid on the *o*-nitroaldehyde, crystallises from acetic acid in colourless needles and melts at  $175^{\circ}$ .

Cuminaldehyde is formed in good yield from cumene by the carbon monoxide method. The *azine*,  $C_{20}H_{24}N_2$ , crystallises in yellow needles and melts at  $118^{\circ}$ .

*Diphenyl-4-aldehyde*,  $C_{13}H_{10}O$ , prepared from diphenyl, crystallises from light petroleum, melts at  $60$ – $61^{\circ}$ , and when oxidised by potassium permanganate yields diphenyl-4-carboxylic acid, which is reduced by hydriodic acid and red phosphorus, forming 4-methyldiphenyl. This crystallises in colourless leaflets and melts at  $47$ – $48^{\circ}$  (Carnelly, this Journal, 1876, i, 13). The *oxime*,  $C_{13}H_{10}NOH$ , forms colourless needles and melts at  $149$ – $150^{\circ}$ ; the *phenylhydrazone*,  $C_{19}H_{16}N_2$ , crystallises in slightly yellow needles and melts at  $188$ – $189^{\circ}$ ; the *aniline* derivative,  $C_6H_4Ph\cdot CH:NPh$ , crystallises in colourless leaflets and melts at  $150$ – $151^{\circ}$ .

*Hydrindene-5-aldehyde*,  $CH_2<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>C_6H_3\cdot CHO$ , is formed in a 25 per cent. yield from hydrindene, together with an *oil* which has an odour of roses and boils at  $168^{\circ}$  under 18 mm. pressure, and a *substance*,  $C_{17}H_{18}O$ , which crystallises in colourless leaflets, melts at  $83^{\circ}$ , boils at  $192^{\circ}$  under 18 mm. pressure, is soluble in aqueous alkali hydroxides, and is precipitated from its alkaline solution by carbon dioxide.

The *aldehyde* forms a colourless oil which boils at  $255$ – $257^{\circ}$ , and is



oxidised by potassium permanganate, forming trimellitic acid, or slowly by air, forming *hydrindene-5-carboxylic acid*,  $C_{10}H_{10}O_2$ . This crystallises in microscopic prisms and melts at  $177^\circ$ . The aldehyde forms an *oxime*,  $C_{10}H_{11}ON$ , crystallising in colourless leaflets and melting at  $65^\circ$ ; an *azine*,  $C_{20}H_{20}N_2$ , crystallising in yellow needles and melting at  $162^\circ$ ; and an *aniline* derivative,  $C_{16}H_{15}N$ , crystallising in stellate aggregates of needles and melting at  $85^\circ$ . G. Y.

**A New Reaction of Aldehydes.** Action of *iso*Hydroxycarbamide on Benzaldehyde, and Properties of Benzylidenecarbamidoxime. Action of Water on Benzylidenecarbamidoxime. A. CONDUCHÉ (*Bull. Soc. chim.*, 1906, [iii], 35, 418—430 and 431—435).—Most of the data given in the first paper have been recorded already (Abstr., 1905, i, 288). The products of the action of hydrochloric acid on benzylidenecarbamidoxime are now given as benzonitrile and ammonium chloride (compare *loc. cit.*). It is also found that the product of the action of alcoholic or aqueous alkalis on benzylidenecarbamidoxime is  $\alpha$ -benzaldoxime, and not the  $\beta$ -isomeride as previously supposed (*loc. cit.*). Potassium cyanate condenses immediately with  $\beta$ -benzaldoxime hydrochloride to form benzylidenecarbamidoxime. The same condensation product is formed when potassium cyanate reacts with  $\alpha$ -benzaldoxime, but only in presence of nitric acid (compare *loc. cit.*).

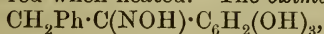
In the second paper it is shown that when benzylidenecarbamidoxime is boiled with water or when heated in closed tubes with water at  $120^\circ$  or at  $160$ — $220^\circ$  the same products are formed, namely,  $\alpha$ -benzaldoxime, benzamide, benzonitrile, and carbamide, the relative proportions of these substances formed depending on the temperature employed.

T. A. H.

**Action of Nitrogen Tetroxide on Benzaldoxime.** GIACOMO PONZIO (*J. pr. Chem.*, 1906, [ii], 73, 494—496. Compare Beckmann, Abstr., 1889, 980; Scholl, Abstr., 1891, 315).—The action of 1 mol. of nitrogen tetroxide on 1 mol. of benzaldoxime in ethereal solution leads to the formation of benzaldoxime peroxide and diphenylglyoxime peroxide in yields of 15 per cent., and of phenyldinitromethane in a yield of 50 per cent. of the theoretical, whilst the action of 2 mols. of nitrogen tetroxide leads to the formation of phenyldinitromethane in a yield of 75 per cent. of the benzaldoxime, no peroxide being formed.

G. Y.

**Phenylacetic Acid. Ketone Dyes. Trihydroxydeoxybenzoin and its Derivatives.** EMILIO NOELTING and VIKTOR KADIERA (*Ber.*, 1906, 39, 2056—2060).—*Phenylgallacetophenone* (*trihydroxydeoxybenzoin*),  $CH_2Ph \cdot CO \cdot C_6H_2(OH)_3$ , obtained by heating together phenylacetic acid, pyrogallol, and zinc chloride at  $150^\circ$  for thirty minutes, crystallises from water, in which it is somewhat sparingly soluble, as pale yellow prisms melting at  $141$ — $142^\circ$ . It dissolves readily in most organic solvents and in dilute potassium hydroxide, giving a yellow solution which turns red when heated. The *oxime*,



crystallises in pale yellow needles melting at  $166^{\circ}$ . It dissolves sparingly in chloroform, and its solutions in alkali hydroxides are first yellow, but rapidly turn green. The isomeric *isonitroso*-derivative,  $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OH})_3$ , obtained by the action of nitrous acid on the ketone, crystallises from dilute alcohol in bright yellow cubes melting at  $144^{\circ}$  and soluble in hot water and most organic solvents.

The *diisonitroso*-derivative,  $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}_6\text{H}_2(\text{OH})_3$ , forms colourless crystals melting at  $168^{\circ}$  and dissolves readily in alcohol or glacial acetic acid; when boiled with dilute hydrochloric acid, it yields *trihydroxybenzil*,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OH})_3$ , which crystallises from hot water in colourless needles melting at  $143^{\circ}$  and readily soluble in most solvents.

J. J. S.

**1:4-Anthraquinone.** CARL LIEBERMANN (*Ber.*, 1906, 39, 2089—2090).—A reply to Lagodzinski (this vol., i, 439). C. S.

The Products of the Action at a High Temperature of Sodium *iso*Butoxide or Propoxide on Camphor. ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1906, 142, 1309—1313. Compare *Abstr.*, 1892, 72).—*iso*Butylcamphol,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{CHMe}_2 \\ | \\ \text{CH}\cdot\text{OH} \end{smallmatrix}$ , ob-

tained by heating sodium *isobutoxide* and camphor in an autoclave at  $220$ — $230^{\circ}$  for twenty-four hours, forms opaque, white crystals, distils between  $235^{\circ}$  and  $255^{\circ}$ , melts at  $55^{\circ}$ , and has  $[\alpha]_D + 20\cdot7^{\circ}$  in alcoholic solution; the *acetate* boils at  $135^{\circ}$  under 20 mm. pressure. *iso*Butylcamphor,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{CHMe}_2 \\ | \\ \text{CO} \end{smallmatrix}$ , obtained by oxidising *isobutylcamphol*

by means of potassium permanganate, melts at  $28^{\circ}$ , and has  $[\alpha]_D + 72\cdot4^{\circ}$  in alcoholic solution. When heated with bromine in sealed tubes at  $100^{\circ}$  it yields *isobutylidenecamphor*,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C}\cdot\text{CH}\cdot\text{CHMe}_2 \\ | \\ \text{CO} \end{smallmatrix}$ , an oily liquid

which boils at  $145^{\circ}$  under 10 mm. pressure, has  $[\alpha]_D + 114\cdot4^{\circ}$ , and yields *isobutyric* and *camphoric* acids on oxidation. The *nitrosate*,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C}\cdot\text{C}_4\text{H}_8\text{O}_4\text{N}_2 \\ | \\ \text{CO} \end{smallmatrix}$ , formed by the action of concentrated nitric

acid or amyl nitrite and nitric acid, forms thin, white needles, melts with decomposition at  $178^{\circ}$ , is slightly soluble in alcohol and ether, more readily so in boiling benzene or acetone, and has  $[\alpha]_D + 93^{\circ}$ . By the action of dilute potassium hydroxide it is converted into *isonitrosohydroxyisobutylcamphor*,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C}(\text{OH})\cdot\text{C}(\text{C}_3\text{H}_7)\cdot\text{NOH} \\ | \\ \text{CO} \end{smallmatrix}$ , which crystallises from a mixture of ether and light petroleum in the form of thin, white needles melting at  $95^{\circ}$ .

*Propylcamphol*,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CHPr}^a \\ | \\ \text{CH}\cdot\text{OH} \end{smallmatrix}$ , prepared in similar manner to the corresponding *isobutyl* compound, crystallises from methyl alcohol, melts at  $61^{\circ}$ , and has  $[\alpha]_D + 12\cdot5^{\circ}$ ; the *acetate* boils at  $120^{\circ}$  under 10 mm. pressure and solidifies at  $0^{\circ}$ . *Propylcamphor*,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CHPr}^a \\ | \\ \text{CO} \end{smallmatrix}$ , is a liquid which

boils at  $123^{\circ}$  under 14 mm. pressure and has  $[\alpha]_D + 55.6^{\circ}$ . *Propylidene-camphor*,  $C_8H_{14} \begin{smallmatrix} \diagup C:CH \cdot CH_2Me \\ \diagdown CO \end{smallmatrix}$ , is a liquid which has  $[\alpha]_D + 87^{\circ}$  and has not yet been obtained quite pure, but which yields the *nitrosate*,  $C_8H_{14} \begin{smallmatrix} \diagup C:C_3H_6O_4N_2 \\ \diagdown CO \end{smallmatrix}$ , melting and decomposing at  $160^{\circ}$ .

M. A. W.

**Carvone. III. The Semicarbazones of Carvone.** HANS RUPE and KARL DORSCHKY (*Ber.*, 1906, 39, 2112—2115. Compare Abstr., 1905, i, 449; this vol., i, 374).—The carvone semicarbazone melting at  $141$ — $142^{\circ}$  (Knoevenagel and Samel, this vol., i, 296) was obtained two years ago by the authors by adding to a concentrated aqueous solution of semicarbazide hydrochloride, carvone, alcohol, and finally potassium acetate, rise of temperature being carefully avoided; without this precaution and by using sodium hydrogen carbonate in the place of potassium acetate, the semicarbazone which melts at  $162$ — $163^{\circ}$  (Baeyer, Abstr., 1894, i, 535) is obtained. Both forms are crystallographically identical and mutually convertible, the former changing completely into the latter by prolonged boiling in methyl-alcoholic solution or by careful heating at  $170$ — $175^{\circ}$ ; the latter isomeride is only partially converted into the former in boiling methyl alcohol, the complete transformation being observed only once in the case of a specimen which had been kept for a year. The two isomerides are soluble in the ordinary organic solvents, sparingly in the cold, easily on warming.

The isomeride with the higher melting point is unchanged in pyridine solution; the other changes sufficiently slowly to enable its rotatory power to be measured. The former has  $[\alpha]_D 11.50^{\circ}$  and the latter  $11.30^{\circ}$  at  $20^{\circ}$ . The specific rotation of the latter is constant for a short time, and then suddenly changes to another constant value about five minutes smaller.

[With WALTER HOTZ.]—The semicarbazones are monoclinic  $[a:b:c = 0.50550:1:0.4706; \beta = 83^{\circ}26']$ . C. S.

**Aroma of Natural Musk.** HEINRICH WALBAUM (*J. pr. Chem.*, 1906, [ii], 73, 488—493).—When distilled with steam, crude musk yields 1.4 per cent. of a dark brown oil, about half of which distils at  $200$ — $210^{\circ}$  under 9 mm. pressure.

*Muskone*,  $C_{15}H_{28}O$  or  $C_{16}H_{30}O$ , is obtained by treating the distillate with alcoholic potassium hydroxide and distilling the product at  $160$ — $164^{\circ}$  under 7 mm. pressure. It is a colourless, viscid oil, which has a strong but pleasant odour of musk, boils at  $142$ — $143^{\circ}$  under 2 mm., or with slight decomposition at  $327$ — $330^{\circ}$  under 752 mm. pressure, has a sp. gr. 0.9268 at  $15^{\circ}$ ,  $n_D 1.479$  at  $25^{\circ}$  or 1.4844 at  $15^{\circ}$ , and  $[\alpha]_D - 10^{\circ}6'$ . It is only sparingly soluble in water, but readily so in alcohol, does not form an additive compound with sodium hydrogen sulphite, and does not give a red coloration with rosaniline decolorised by sulphur dioxide.

The *oxime* crystallises in needles and melts at  $46^{\circ}$ . The *semi-*



*carbazone*,  $C_{16}H_{31}ON_3$  or  $C_{17}H_{33}ON_3$ , crystallises in slender, white prisms, melts at  $133-134^\circ$ , and is odourless, but gives an odour of musk when heated with dilute sulphuric acid. Muskone is not identical with Bauer's ketone musk (Abstr., 1898, i, 523).

The fraction boiling at  $65-106^\circ$  under 7 mm. pressure, obtained in the purification of muskone, has an unpleasant odour and gives the pine-wood reaction for pyrrole. G. Y.

**Copaiba Balsam from Surinam.** LEOPOLD VAN ITALLIE and C. H. NIEUWLAND (*Arch. Pharm.*, 1906, 244, 161-164. Compare Abstr., 1904, i, 1037).—The bulk of the resin is soluble in 5 per cent. aqueous sodium carbonate; the resin-acid has an acid number 171 and saponification number 178, and cannot be crystallised or separated into different acids by fractional precipitation of its salts. The *resen* cannot be crystallised.

From the sesquiterpene alcohol, which melts at  $114-115^\circ$  when purified, a *sesquiterpene* was obtained, of which the molecular weight corresponds with the formula  $C_{15}H_{24}$ ; it is a mobile liquid which boils at  $252^\circ$  under 759 mm. pressure, has a sp. gr., 0.952 at  $15^\circ$ ,  $n_D$  1.5189 at  $15^\circ$ , and  $[\alpha]_D - 61.7^\circ$ ; in the air, it soon changes to a resinous solid. C. F. B.

**Formula of Elaterin.** ARMAND BERG (*Bull. Soc. chim.*, 1906, [iii], 35, 435-437. Compare Abstr., 1898, ii, 447).—Elaterin has the formula  $C_{28}H_{38}O_7$ , yields a *diacetyl* derivative, and on hydrolysis with potassium hydroxide in alcohol furnishes acetic acid (1 mol.) and *elateridin*. The latter, by the further action of the alkali, yields *elateric acid*. These products are all amorphous and non-volatile. T. A. H.

**Curcumin.** C. LORING JACKSON and LATHAM CLARKE (*Ber.*, 1906, 39, 2269-2270. Compare Abstr., 1905, i, 804).—As a result of Zeisel determinations with curcumin, it is concluded that the formula for curcumin is  $C_{14}H_{14}O_4$ , and not  $C_{21}H_{20}O_6$ , that assigned to it by Ciamician and Silber. A. McK.

**Condensation of Gallocyanin Dyes with Aminosulphonic Acids.** EUGÈNE GRANDMOUGIN (*Zeit. Farb. Ind.*, 1906, 5, 201).—Gallocyanin dyes condense with aminosulphonic acids, when warmed with them in aqueous suspension, to form dyes which are bluer in colour than the original substances; the condensation of prune (Sandoz) with sulphanilic acid is described in detail. Naphthionic acid, *o*-toluidinesulphonic acid, *p*-toluidinesulphonic acid, and  $\beta\beta$ -naphthyl-aminesulphonic acid can be used in place of sulphanilic acid, but dimethylmetanilic acid does not condense with the dyes, a free aminoradicle apparently being essential for the condensation. W. A. D.

**Tannins.** EDUARD STRAUSS and BERNHARD GSCHWENDNER (*Zeit. angew. Chem.*, 1906, 19, 1121-1125).—*Quebracho tannin*,  $[C_{41}H_{44}O_{18}(OMe)_2]_2$ , was obtained from the bark of *Quebracho colorada* by extracting first with chloroform and then with alcohol. On adding water to the

alcoholic extract and warming, phlobaphens are deposited from the solution, which are then removed by shaking the solution with Tripoli powder. On concentrating the solution in a vacuum, the tannin was precipitated by means of lead acetate, the lead salt after filtration being then suspended in water and decomposed with hydrogen sulphide. The aqueous solution so obtained was then evaporated in a vacuum, and the residue taken up in the least amount of alcohol and poured into absolute ether. By this means, the tannin was obtained in the form of light flakes which were rapidly dried in a vacuum over sulphuric acid and phosphoric oxide; it at once becomes sticky on exposure to moist air. Analyses agreed with the formula  $C_{43}H_{50}O_{20}$ , which is the formula given by Schuett to the tannin from quinine.

By heating the tannin with a mixture of acetic anhydride and glacial acetic acid, an *acetyl* derivative is obtained, which, however, has the formula  $(C_{30}H_{22}O_{11}Ac_6)_2$ , forms a white powder which is fairly readily soluble in alcohol, very soluble in acetone, ethyl acetate, glacial acetic acid, or acetic anhydride, but is insoluble in water, ether, or benzene. The corresponding *benzoyl* derivative,  $(C_{30}H_{22}O_{11}Bz_6)_2$ , is a white solid; it darkens at  $200^\circ$  and decomposes at  $215^\circ$ . An aqueous solution of the tannin allowed to remain for two days with a solution of formaldehyde deposited a dark red substance which could not be further purified. When reduced with sodium amalgam, the tannin yields a compound of the formula  $(C_{30}H_{25}O_{11})_2$ .

*Maletto tannin*,  $(C_{43}H_{50}O_{20})_2$ , was obtained from finely-powdered Maletto bark by extraction with 96 per cent. alcohol. From its analysis and properties it appears to be identical with Quebracho tannin.

*Tannin from tea*,  $(C_9H_{10}O_5)_x$ , was obtained from finely-powdered black tea by first extracting it with chloroform and then with alcohol, and proceeding with the extraction and purification already described. It forms an almost white powder. If lead acetate is used in the purification, a compound of the formula  $C_{13}H_{19}O_{10}$  is obtained.

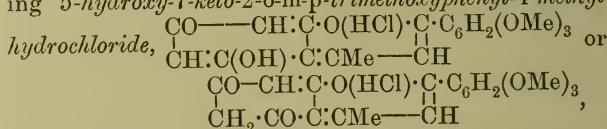
*Sumach tannin*,  $(C_{16}H_{15}O_{11})_x$ , was prepared according to Loewe's instructions. A determination of methoxyl showed that the formula should be  $C_{32}H_{29}O_{11} \cdot OMe$ . P. H.

**Iodotannin.** VIGNERON (*J. Pharm. Chim.*, 1906, [vi], 23, 469—471).—A two per cent. solution of tannin in water to which one per cent. of iodine has been added gives a brown precipitate with sodium hydrogen carbonate, a red coloration with potassium cyanide, a red coloration, slight precipitate, and free iodine on addition of nitric acid containing nitrous acid, and when this is followed by potassium cyanide, the red coloration changes to yellow, and a thick, white precipitate is formed.

A similar solution of iodogallic acid gives a black precipitate with sodium hydrogen carbonate, and no precipitate on the addition of nitric acid containing nitrous acid, and followed by potassium cyanide. The reaction with potassium cyanide alone is similar to that with the iodotannin solution. The author is of opinion that iodotannin extracts recently sold in France for making galenical preparations are prepared from gallic acid and not from tannin. T. A. H.

**Formation of Methronic Acid.** GEORG SCHROETER (*Ber.*, 1906, 39, 2129—2131).—A claim for priority and a criticism of Trepheleff's views regarding the mechanism of the formation of methronic acid (this vol., i, 528).  
A. McK.

**Quinonoid Benzopyran Derivatives.** CARL BÜLOW and CARL SCHMID (*Ber.*, 1906, 39, 2027—2033. Compare this vol., i, 201, 300).—Phloroglucinol condenses with 2:3:4-trimethoxybenzoylacetone in the presence of hydrogen chloride in acetic acid solution, yielding 5-hydroxy-7-keto-2-o-m-p-trimethoxyphenyl-4-methyl-1:4-benzopyran hydrochloride,

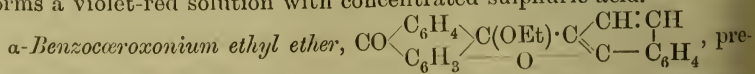


which crystallises from alcohol containing a small amount of hydrogen chloride in long, dark yellow needles containing  $1\text{H}_2\text{O}$ . The salt is partially hydrolysed in aqueous solution, and melts and decomposes at  $218\text{--}219^\circ$ . The *sulphate*,  $\text{C}_{19}\text{H}_{18}\text{O}_6 \cdot \text{H}_2\text{SO}_4 \cdot \text{C}_2\text{H}_6\text{O}$ , melts at  $216\text{--}217^\circ$ ; the alcohol of crystallisation is removed by prolonged heating at  $100^\circ$ . When crystallised from alcohol containing 25 per cent. of sulphuric acid, a *sulphate*,  $\text{C}_{19}\text{H}_{18}\text{O}_6 \cdot 2\text{H}_2\text{SO}_4$ , which crystallises in orange needles melting at  $155\text{--}156^\circ$ , is obtained. The *picrate*,  $\text{C}_{25}\text{H}_{21}\text{O}_{13}\text{N}_3$ , forms orange needles, changes colour at  $100^\circ$ , and melts and decomposes at  $219\text{--}220^\circ$ . The *base*,  $\text{C}_{19}\text{H}_{18}\text{O}_6 \cdot \text{H}_2\text{O}$ , forms small, brownish-red needles, softens at  $140\text{--}145^\circ$ , and is insoluble in ether and only sparingly soluble in benzene. It cannot be acetylated, but yields an *oxime*,  $\text{C}_{19}\text{H}_{19}\text{O}_6\text{N}$ , melting at  $132\text{--}136^\circ$ , and a *phenylhydrazone*,  $\text{C}_{31}\text{H}_{30}\text{O}_4\text{N}_2$ , which crystallises from alcohol in plates and melts at  $113\text{--}114^\circ$ .

When the hydrochloride is heated with concentrated hydrochloric acid at  $150\text{--}180^\circ$ , it yields 5-hydroxy-7-keto-2-o-m-p-trihydroxyphenyl-4-methyl-1:4-benzopyran hydrochloride,  $\text{C}_{16}\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O} \cdot \text{HCl}$ , in the form of flesh-red, flat needles melting at  $288^\circ$ . The corresponding *base*,  $\text{C}_{16}\text{H}_{12}\text{O}_6$ , crystallises in dark brown, slender needles with a green lustre; it does not melt below  $300^\circ$ , and is insoluble in ether or benzene.  
J. J. S.

**Benzocæroxonium Compounds.** EDUARD LAUBE (*Ber.*, 1906, 39, 2245—2249).—*Erythroxyanthraquinone α-naphthol ether* [1-*α-naphthoxyanthraquinone*],  $\text{C}_{24}\text{H}_{14}\text{O}_3$ , prepared by heating a mixture of potassium anthraquinone-1-sulphonate and potassium *α*-naphthoxide for eight hours at  $150\text{--}160^\circ$ , separates from light petroleum in yellow crystals and melts at  $275\text{--}276^\circ$ . When warmed with concentrated sulphuric acid, it forms a purple solution.

1-*β-Naphthoxyanthraquinone*, prepared in an analogous manner, forms a violet-red solution with concentrated sulphuric acid.



prepared by heating 1-*α*-naphthoxyanthraquinone with 70 per cent. sulphuric acid at  $150^\circ$ , separates from alcohol in colourless leaflets and



melts at 197—198°. The *ferrichloride*,  $C_{24}H_{13}O_2Cl, FeCl_3$ , of the base decomposes at 240°.

*β-Benzoceroxonium ethyl ether*,  $CO \begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_3 \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} C(OEt) \cdot C \begin{array}{c} \diagup C_6H_4 \\ \diagdown C \cdot CH \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} CH$ ,

melts at 193—194°. The *ferrichloride* of the corresponding base melts at 240°.

*Acetyl-α-benzoceroxonol*,  $C_{26}H_{16}O_3$ , prepared by reducing benzoceroxonium salts by zinc dust and glacial acetic acid and then acetylating the product, separates from alcohol in yellow crystals. *Acetyl-β-benzoceroxonol* is brownish-yellow and melts at 195—200°.

By further reducing the benzoceroxonol compounds with hydriodic acid a small amount of *benzoceroxene* is obtained with other products.

A. McK.

**Aconitine and Aconine from Aconitum Napellus.** HEINRICH SCHULZE (*Arch. Pharm.*, 1906, 244, 136—159, 165—196).—The first seventeen pages contain an historical account of previous researches. The results of the present research have already been published in part (*Abstr.*, 1905, i, 656).

Purified aconitine, melting at 197—198° and identical in crystalline form with that analysed by Dunstan and Ince (*Trans.*, 1891, 278—281), was found to have a composition corresponding, not with the formula proposed by these investigators or with that of Wright, but with those proposed by Freund and Beck,  $C_{34}H_{47}O_{11}N$  or  $C_{34}H_{45}O_{11}N$  (*Abstr.*, 1894, i, 263). The hydrobromide was obtained crystallised from a mixture of alcohol and ether with  $\frac{1}{2}H_2O$ , when it melted and decomposed at 206—207°, and also crystallised with  $2\frac{1}{2}H_2O$ ; the *α*-aurichloride, melting at 136·5°, crystallised with  $3H_2O$ . Aconitine is best hydrolysed by heating with water in an autoclave under 6—7 atmospheres pressure; the yield of aconine hydrochloride was 85 per cent. of the theoretical.

The tetra-acetyl derivative of picroaconitine (benzoylaconine) is not different from the triacetyl derivative of aconitine (acetylbenzoylaconine), as Dunstan and Carr thought (*Trans.*, 1895, 461, 462); the two substances melt at 207—208° and are identical. Aconine does not form a quaternary ammonium salt with methyl iodide or sulphate, or an amino-oxide with hydrogen peroxide. Aconine hydrochloride and hydrobromide, melting at 175—176° and 225°, were obtained crystallised with 2 and  $1\frac{1}{2}H_2O$  respectively.

When aconitine is heated with methyl alcohol at 120—130°, the acetyl group is eliminated as acetic acid, but instead of picroaconitine *methylpicroaconitine* is obtained; the *hydrobromide* and *hydrochloride* of this crystallise each with  $3H_2O$  and melt at 188—189° and 190° respectively; the base, which also is crystalline, is hydrolysed to aconine, benzoic acid, and methyl alcohol when it is heated with a large excess of water at 150—160° for twenty-four hours, the hydrolysis taking place much less readily than in the case of aconitine, where heating for six hours suffices. When aconitine is heated with ethyl alcohol, *ethylpicroaconitine* is formed, but in worse yield than *methylpicroaconitine*.

Aconine hydrobromide crystallises with  $1\frac{1}{2}\text{H}_2\text{O}$ , and melts and decomposes at about  $225^\circ$ . With bromine, the alkaloid forms a perbromide, but no addition or substitution product. Neither aconine nor aconitine, nor the tetra-acetyl derivative of the latter, decolorises potassium permanganate rapidly in dilute sulphuric acid solutions.

Alkaline permanganate or chromic acid oxidises aconine with formation of aldehyde, and, in the latter case, of methylamine. In the former case, the main product was amorphous. In the latter case, the main product, which was both acid and basic, could not be obtained crystalline; a portion had basic properties, and from this a crystalline hydrochloride,  $\text{C}_{24}\text{H}_{35}\text{O}_8\text{N}\cdot\text{HCl}$  (or  $\text{C}_{24}\text{H}_{37}\text{O}_8\text{N}\cdot\text{HCl}$ ), with  $3\text{H}_2\text{O}$ , melting at  $213^\circ$ , was obtained. C. F. B.

**Old Decomposed Cocaine Hydrochloride.** PIERRE BRETEAU (*J. Pharm. Chim.*, 1906, [vi], 23, 474—476).—In a sample, obviously decomposed, of this alkaloidal salt made in 1891, methyl benzoate, benzoic acid, and ecgonine hydrochloride were found. The decomposition is attributed to the presence of a small quantity of water in the original salt. T. A. H.

**Derivatives of Caffeine and Reactions of its Glyoxaline Nucleus.** BRISSEMORET (*Bull. Soc. chim.*, 1906, [iii], 35, 316—321).—When a mixture of caffeine and salicylic acid in molecular proportions is dissolved in boiling water, there separates on cooling colourless, acicular crystals of the compound  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\cdot\text{C}_7\text{H}_6\text{O}_3$ . An analogous product is obtained with protocathecuic or gallic acid.

Similar compounds may be obtained of 3:7-dimethylxanthine and gallic and salicylic acids and of 1:3-dimethylxanthine and gallic acid.

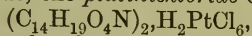
All these compounds dissolve on adding sodium hydroxide to their suspensions in water, and the bases may be then either filtered out or dissolved out by an appropriate solvent. It is possible to determine their composition by this means. The author regards the formation of these compounds as due to the influence of the glyoxaline ring in caffeine, and as evidence for the accuracy of this view points out that similar combinations may be brought about between glyoxaline itself and gallic or salicylic acid and that each of these may be isolated in a crystalline condition by mixing a solution of the base in ether with a like solution of the appropriate acid. T. A. H.

**Behaviour of Cotarnine towards Grignard's Reagent.** MARTIN FREUND and HANS HERMANN REITZ (*Ber.*, 1906, 39, 2219—2237. Compare Abstr., 1904, i, 187).—1-Ethylhydro-

cotarnine,  $\text{CH}_2 \begin{array}{c} \text{O}\cdot\text{C}:\text{C}(\text{OMe})\cdot\text{C}\cdot\text{CHEt}\cdot\text{NMe} \\ \text{O}\cdot\text{C}:\text{CH}—\text{C}\cdot\text{CH}_2—\text{CH}_2 \end{array}$ , prepared by the

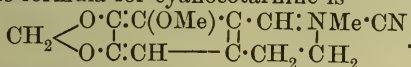
action of magnesium ethyl iodide on cotarnine, separates from dilute alcohol in rhombic pyramids and melts at  $59\text{--}60^\circ$ . Its hydrochloride crystallises in needles and melts at  $215\text{--}216^\circ$ ; its dichromate crystallises in rhombic plates, whilst its methiodide separates from alcohol in hexagonal plates and melts at  $188\text{--}189^\circ$ . The 5-bromo derivative,  $\text{C}_{14}\text{H}_{18}\text{O}_3\text{NBr}$ , separates from light petroleum in octagonal plates and melts at  $104^\circ$ ; the orientation of the bromine atom as indicated is correct, since the same compound is formed when

magnesium ethyl iodide acts on bromocotarnine. When  $\alpha$ -ethylcotarnine is oxidised with hydrogen peroxide, it is converted into the corresponding amino-oxide, the *platinichloride* of which,

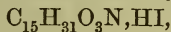


forms tetragonal plates and melts at  $196-197^\circ$ .

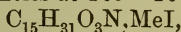
Attempts to prepare methoxyl derivatives of benzyl  $\alpha$ -hydrocotarnine by the action of magnesium alkyl halides on cyanocotarnine failed; when magnesium ethyl iodide, for example, acts on cyanocotarnine, ethyl hydrocotarnine is produced, a result which indicates that the probable formula for cyanocotarnine is



1-Propylhydrocotarnine,  $\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$ , prepared by the action of magnesium propyl iodide on cotarnine, separates from light petroleum in tetragonal pyramids and melts at  $66-67^\circ$ . Its *hydriodide*,



forms rhombic plates and melts at  $165-166^\circ$ . Its *methiodide*,

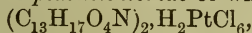


separates from alcohol in tetragonal crystals and melts at  $165-166^\circ$ .

1-isoPropylhydrocotarnine *hydriodide*,  $\text{C}_{15}\text{H}_{31}\text{O}_3\text{N}, \text{HI}$ , separates from alcohol in rhombic plates and melts at  $196-197^\circ$ .  $\alpha$ -isoPropylhydrocotarnine *methiodide* separates from alcohol in needles and melts at  $144-145^\circ$ .

1-isoButylhydrocotarnine,  $\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}$ , separates from light petroleum in tetragonal pyramids and melts at  $46-47^\circ$ . Its *hydrochloride* separates from water in octagonal crystals and melts at  $217-218^\circ$ ; its *platinichloride* melts and decomposes at  $208-209^\circ$ ; its *hydrobromide* melts at  $205-206^\circ$ ; its *methiodide* separates from alcohol in hexagonal plates and melts at  $189-190^\circ$ .

When 1-methylhydrocotarnine is oxidised by hydrogen peroxide, it forms an amino-oxide, the *platinichloride* of which,



crystallises from dilute alcohol in plates and melts at  $198^\circ$ , whilst the corresponding *hydriodide* melts at  $116^\circ$ .

1-Phenylhydrocotarnine,  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}$ , prepared from magnesium phenyl iodide and cotarnine cyanide, separates from light petroleum in pyramids and melts at  $97-98^\circ$ . It may also be prepared from cotarnine hydrochloride and magnesium phenyl iodide.

1-p-Methoxylphenylhydrocotarnine,  $\text{C}_{19}\text{H}_{21}\text{O}_4\text{N}$ , is a viscid oil.

1- $\alpha$ -Naphthylhydrocotarnine,  $\text{C}_{22}\text{H}_{21}\text{O}_3\text{N}$ , melts at  $120-122^\circ$ ; its *hydrobromide* separates from dilute alcohol in cubes and melts at  $253^\circ$ .

1-Benzylhydrocotarnine,  $\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}$ , separates from light petroleum in rhombic plates and melts at  $70^\circ$ . Its *hydriodide* separates from alcohol in plates and melts at  $217-218^\circ$ .

*Di-hydrocotarnine*,



prepared by the action of magnesium acetylene tetrabromide on cotarnine, crystallises from water in rhombohedra and melts at  $163-164^\circ$ . The *hydrobromide*,  $\text{C}_{24}\text{H}_{28}\text{O}_6\text{N}_2, 2\text{HBr}, 2\text{H}_2\text{O}$ , crystallises



from water in rhombic needles and, when dehydrated, melts at 233—234°; the *hydrochloride*,  $C_{24}H_{28}O_6N_2 \cdot 2HCl \cdot 2H_2O$ , separates from water in silky, rhombic leaflets and melts at 231—232°; the *hydriodide*,  $C_{24}H_{28}O_6N_2 \cdot 2HI$ , separates from alcohol in needles and melts at 234—235°. The *hydrogen sulphate*,  $C_{24}H_{28}O_6N_2 \cdot 2H_2SO_4 \cdot 2H_2O$ , crystallises from water in pyramids and melts and decomposes at 236—237°; the *methiodide*,  $C_{24}H_{28}O_6N_2 \cdot MeI$ , crystallises from water in needles and melts at 233—234°.

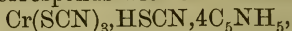
Di-hydrocotarnine may also be obtained by the action on cotarnine of the magnesium compounds of alkyl iodides, methylene chloride, benzylidene chloride, ethylene bromide, and piperonyl chloride respectively.

*p*-Cyanobenzyl iodide, prepared by the action of potassium iodide on *p*-cyanobenzyl chloride, separates from alcohol in needles and melts at 143—144°. It does not form a magnesium compound.

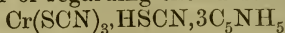
The physiological action of a number of the compounds described has been tested. A. McK.

**Conversion of Ephedrine into  $\psi$ -Ephedrine.** ERNST SCHMIDT (*Arch. Pharm.*, 1906, 244, 239—240. Compare Abstr., 1904, i, 769).—A much better yield of  $\psi$ -ephedrine is obtained by heating ephedrine hydrochloride with ten times its weight of 25 per cent. hydrochloric acid for twelve hours in the water-bath. Even then the conversion is not complete; it seems that equilibrium is reached between the two substances. C. F. B.

**Tetrathiocyanodipyridinechromium Salts.** PAUL PFEIFFER and W. OSANN (*Ber.*, 1906, 39, 2115—2125).—*Pyridinium tetrathiocyanodipyridinechromiates*.—When dry potassium or ammonium chromothiocyanate is heated on the water-bath with anhydrous pyridine for four hours, a substance is obtained which separates from a small quantity of hot pyridine in glistening, dark red, prismatic crystals, stable in the air; it corresponds with the formula

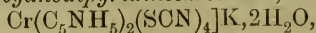


but does not give a coloration with ferric chloride. At 100° it loses 1 mol.  $C_5NH_5$ , yielding a substance,  $Cr(SCN)_3 \cdot HSCN \cdot 3C_5NH_5$ , which again takes up 1 mol.  $C_5H_5N$  by crystallisation from this solvent. Sand and Burger's formula (this vol., i, 487) is rejected, and arguments are advanced in favour of regarding the substance



as the normal additive compound of 1 mol.  $C_5H_5N$  and the acid  $[Cr(C_5NH_5)_2(SCN)_4]H$ ; the substance  $Cr(SCN)_3 \cdot HSCN \cdot 4C_5NH_5$  is regarded as belonging to the class of the anomalous ammonium salts (compare Werner, Abstr., 1903, i, 234). When either of the compounds suspended in cold water is treated with chlorine, a *dihydroxylochloride*,  $[Cr(C_5NH_5)_2(OH)_2(OH)_2]Cl$ , is obtained; potassium hydroxide eliminates the pyridine, and by subsequent treatment with concentrated hydrochloric acid pure tetra-aquodipyridinechromium chloride is obtained.

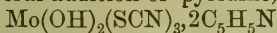
*Potassium tetrathiocyanodipyridinechromiate*,



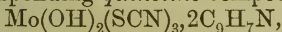
is the chief product of the reaction between anhydrous pyridine and potassium chromothiocyanate; after crystallisation from hot water, it is obtained as a stable, red powder. It can also be crystallised from aniline or quinoline, does not react with ferric chloride, and is decomposed by chlorine in the presence of cold water with the formation, ultimately, of tetra-aquodipyridinechromium chloride. When the dried substance is crystallised from pyridine, an additive *compound*,  $[\text{Cr}(\text{C}_5\text{NH}_5)_2(\text{SCN})_4]\text{K}, 4\text{C}_5\text{NH}_5$ , is obtained in the form of transparent, red crystals, which quickly effloresce in air, but not in an atmosphere of pyridine. Sodium chromothiocyanate yields similar compounds,  $[\text{Cr}(\text{C}_5\text{NH}_5)_2(\text{SCN})_4]\text{Na}, 3\text{H}_2\text{O}$  and  $[\text{Cr}(\text{C}_5\text{NH}_5)_2(\text{SCN})_4]\text{Na}, 4\text{C}_5\text{NH}_5$ .

The  $4\text{C}_5\text{NH}_5$  in these additive compounds is regarded as being in combination with the alkali metal (compare Rosenheim and Löwenstamm, *Abstr.*, 1903, i, 325). C. S.

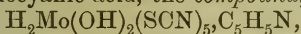
**Halogen Compounds of Molybdenum and Tungsten. II.**  
ARTHUR ROSENHEIM and MORDUCH KOSS (*Zeit. anorg. Chem.*, 1906, 49, 148—156. Compare *Abstr.*, 1905, ii, 717; Weinland and Knoll, *Abstr.*, 1905, ii, 323; Sand and Burger, *Abstr.*, 1905, i, 923; Hofmann and von der Heide, *Abstr.*, 1896, ii, 605).—When molybdenum trioxide,  $\text{MoO}_3$ , is added in excess to a 10 per cent. aqueous solution of thiocyanic acid and the mixture boiled and filtered, a deep red solution is obtained, from which, on the careful addition of pyridine,



can be isolated in the form of brownish-red needles. It is thus shown that, contrary to the generally accepted view, sexavalent molybdenum can be reduced to the quinquevalent state by boiling with thiocyanic acid alone. The corresponding *quinoline* compound,



prepared in an analogous manner, crystallises from absolute alcohol in dark, reddish-brown needles. From a solution of the pyridine compound in excess of thiocyanic acid, the *compound*,

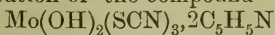


was obtained in black, lustrous, rhombic crystals, readily decomposed by water.

When either of the pyridine compounds is boiled with concentrated hydrogen chloride until all the thiocyanic acid is driven off, dipyridine-pentachloromolybdate,  $\text{H}_2\text{MoCl}_5, 2\text{C}_5\text{H}_5\text{N}$ , is obtained in light green needles. The three *bromides*,  $\text{H}_2\text{Mo}(\text{OH})_2\text{Br}_5, 2\text{C}_5\text{H}_5\text{N}, 2\text{H}_2\text{O}$ ,  $\text{HMo}(\text{OH})_2\text{Br}_4, \text{C}_5\text{H}_5\text{N}$ , and  $\text{H}_2\text{Mo}(\text{OH})_2\text{Br}_5, 2\text{C}_9\text{H}_7\text{N}$ , recently described by Weinland and Knoll (*loc. cit.*), were also prepared and analysed; the formulæ ascribed to them differ slightly from those found by their discoverers.

Concentrated hydriodic acid exerts a reducing action on both the pyridine and quinoline compounds; from the respective solutions the *compounds*  $\text{H}_5\text{Mo}_2\text{I}_{13}, 5\text{C}_5\text{H}_5\text{N}$  and  $\text{H}_3\text{Mo}_2\text{OI}_9, 3\text{C}_9\text{H}_7\text{N}$ , containing quadrivalent molybdenum, were isolated in the form of black, lustrous needles.

From an aqueous solution of the compound



and excess of potassium cyanide, a *compound*,  $\text{K}_5\text{Mo}(\text{OH})_2(\text{CN})_8$ , was

obtained in yellow plates. With a large excess of potassium cyanide, the compounds  $K_4MoO_2(CN)_4 \cdot 10H_2O$ , in violet-red crystals, and  $K_4MoO_2(CN)_4 \cdot 5H_2O$ , already described by Hofmann and von der Heide (*loc. cit.*), were obtained, as well as a new compound,



which forms deep blue needles.

G. S.

**Quinoline Hydrochloride.** Action of Acid Chlorides on Quinoline. OSKAR ECKSTEIN (*Ber.*, 1906, 39, 2135—2138).—Quinoline hydrochloride, prepared by the action of benzoyl chloride or of acetyl chloride on quinoline in the presence of traces of water, has the formula  $(C_9NH_7, HCl)_2 \cdot H_2O$ , the melting point of which agrees with that recorded in the literature, namely,  $94^\circ$ ; *anhydrous quinoline hydrochloride*, however, melts at  $134^\circ$ , whilst its *platinichloride* forms prisms and melts at  $227.5^\circ$ . Its *hydrogen chloride additive compound*,  $(C_9NH_7, HCl)_2 \cdot HCl$ , prepared by passing a current of dry hydrogen chloride into an ethereal solution of quinoline, melts at  $82^\circ$ .

In Einhorn and Holland's acylation method, whereby the acylation of a given compound is conducted by the action of an acid chloride on its solution in a tertiary base, the assumption that an additive compound is formed from the acid chloride and the tertiary base has been adduced by Einhorn and others. The author describes the additive compounds which acetyl chloride and benzoyl chloride respectively form with quinoline.

The compound,  $C_9NH_7, AcCl$ , prepared by allowing a dry ethereal solution of quinoline and acetyl chloride to remain at a low temperature for a considerable time, forms colourless crystals, is unstable and deliquescent, being readily decomposed into quinoline and acetyl chloride.

The compound,  $C_9NH_7, BzCl$ , prepared in an analogous manner, boils at  $105^\circ$  under 12 mm. pressure, is hygroscopic, and assumes a dark red tint on exposure to air. When acted on by water it forms benzoic anhydride, benzoyl chloride, quinoline, and quinoline hydrochloride.

A. McK.

**Kynurine Ethers.** HANS MEYER (*Monatsh.*, 1906, 27, 255—266). Compare this vol., i, 108; Wenzel, *Abstr.*, 1895, i, 70).—The action of sodium methoxide on 4-chloroquinoline in methyl-alcoholic solution at the ordinary temperature for seventeen days, or at  $130^\circ$  for one

hour, leads to the formation of 4-methoxyquinoline,  $C_6H_4 \begin{smallmatrix} C(OMe):CH \\ N====CH \end{smallmatrix}$

which solidifies in a freezing mixture, melts at  $31^\circ$ , commences to boil at  $245^\circ$ , and on continued distillation is converted partially into the  $\psi$ -methyl ether, the mixture boiling above  $360^\circ$ . The methoxyquinoline is soluble in ether but insoluble in water. The *mercurichloride*,  $C_{10}H_9ON, HgCl_2$ , crystallises in long, white needles, melts and decomposes at  $188$ — $190^\circ$ , and is stable towards light; the *platinichloride* forms almost colourless, delicate, glistening scales, and melts and decomposes at  $227$ — $228^\circ$ ; the *aurichloride*,  $C_{10}H_9ON, HAuCl_4$ , forms small, lemon-yellow crystals and melts and decomposes at  $196$ — $197^\circ$ .



When heated at 300—310°, 4-methoxyquinoline is converted completely into the  $\psi$ -methyl ether,  $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{CH} \\ \text{NMe} \cdot \text{CH} \end{smallmatrix}$ , which, when crystallised from water, melts at about 90° and loses water at 110°; the anhydrous substance melts at 143° and is soluble in water or benzene, but is insoluble in ether. When evaporated with hydrochloric acid, it is converted into *kynurine methochloride*, which crystallises in delicate needles and melts at about 178°. The *aurichloride* forms small, light yellow needles and melts at 168—170°; the *platinichloride* crystallises in orange-yellow needles and melts and decomposes at 212°; the crystalline *mercurichloride* melts at 178°.

Wenzel's ethylkynurine (*loc. cit.*) is 4-ethoxyquinoline and not the  $\psi$ -ethyl ether, as it yields ethyl iodide, although slowly, when boiled with hydriodic acid of sp. gr. 1.7. When heated at about 360°, it changes into the  $\psi$ -ethyl ether,  $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{CH} \\ \text{NEt} \cdot \text{CH} \end{smallmatrix}$ , which was isolated as the *aurichloride*. This crystallises in sheaves of lemon-yellow needles and melts and decomposes at 155°.

G. Y.

**Quinaldinic [Quinoline-2-carboxylic] Acid.** EMIL BESTHORN and JOS. IBELE (*Ber.*, 1906, 39, 2329—2334. Compare *Abstr.*, 1905, i, 612; Meyer, *ibid.*, i, 155, 666).—Quinoline-2-carboxylic acid, prepared by Koenigs' method (*Abstr.*, 1899, i, 389), melts and decomposes at 156°. The authors have repeated the preparation of the chloride and have again obtained the substance melting at 97—98° by using freshly prepared thionyl chloride; if recovered thionyl chloride is employed, the reaction follows another course (compare Meyer, *loc. cit.*). The methyl ester melts at 85° and the amide at 132—133°.

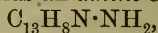
When quinoline-2-carboxylic acid is nitrated at 60—70° with concentrated sulphuric and nitric acids, a mixture of two mononitro-compounds is obtained, which is separated by means of their barium salts. 5-Nitroquinoline-2-carboxylic acid melts and decomposes at 203°, the 8-nitro-compound at 177°. The constitutions are determined by heating them above their melting points, when carbon dioxide is evolved and 5-nitro- and 8-nitro-quinoline respectively are obtained.

C. S.

**Nitro- and Amino-derivatives of  $\alpha$ -Naphthaquinoline and their Oxidation to Quinoline-7:8-dicarboxylic Acid.** RUDOLF HAID (*Monatsh.*, 1906, 27, 315—340).—The two nitro-derivatives of  $\alpha$ -naphthaquinoline described by Claus and Imhoff (*Abstr.*, 1898, i, 333) were mixtures. On repeating the nitration under the same conditions and fractionally crystallising the product from alcohol and benzene, the author obtained four nitro- $\alpha$ -naphthaquinolines. Two of these, melting at 175° and 230° respectively, and constituting together 90 per cent. of the product, have the nitro-group in position 7, 8, 9, or 10, as on reduction and oxidation both yield quinoline-7:8-dicarboxylic acid.

Nitro- $\alpha$ -naphthaquinoline,  $C_{13}H_8N \cdot NO_2$ , melting at 230°, crystallises in glistening, yellow needles, or in aggregates of transparent plates which change slowly into the yellow needles. The *hydrochloride*

crystallises in white needles and melts at  $245\text{--}250^\circ$ ; the *nitrate*,  $\text{C}_{13}\text{H}_8\text{O}_2\text{N}_2\cdot\text{HNO}_3$ , forms slightly yellow, strongly refracting needles or stout prisms and melts at  $220^\circ$ ; the *sulphate* crystallises in glistening needles and melts at  $243^\circ$ . When reduced with stannous chloride and hydrochloric acid, it yields an *amino- $\alpha$ -naphthaquinoline*,



which crystallises from alcohol in thin, colourless, transparent, brittle leaflets or rhombic plates and melts at  $151^\circ$ . The *hydrochloride* forms white prisms, commences to decompose at  $215^\circ$ , and dissolves in water, forming a blood-red solution which has an acid reaction.

*Nitro- $\alpha$ -naphthaquinoline*,  $\text{C}_{13}\text{H}_8\text{O}_2\text{N}_2$ , melting at  $175^\circ$ , crystallises from alcohol in spherical aggregates of long, thin, yellow, glistening needles. The *hydrochloride* crystallises in yellow prisms and melts and decomposes at  $220\text{--}221^\circ$ ; the *nitrate* forms long needles and melts and decomposes at  $193^\circ$ . When reduced with stannous chloride and hydrochloric acid, the nitro-compound yields an *amino- $\alpha$ -naphthaquinoline*, which crystallises in aggregates of yellow leaflets and melts at  $175^\circ$ ; the *hydrochloride* crystallises in long, white, silky needles and commences to decompose at  $230^\circ$ .

*Nitro- $\alpha$ -naphthaquinoline*, melting at  $166^\circ$ , crystallises from alcohol in white needles or leaflets. The *hydrochloride* forms long, delicate, white needles and loses hydrogen chloride above  $100^\circ$ ; the *nitrate* forms yellow needles, commences to decompose at  $125^\circ$ , and is melted at  $150^\circ$ .

*Nitro- $\alpha$ -naphthaquinoline*, melting at  $155^\circ$ , crystallises in long, yellow, glistening needles and is readily soluble in alcohol or benzene. The *hydrochloride* forms yellow, strongly refracting needles and melts and decomposes at  $210\text{--}211^\circ$ ; the *nitrate* forms yellow, strongly refracting needles and melts at  $178^\circ$ .

*Quinoline-7 : 8-dicarboxylic acid*,  $\text{C}_{11}\text{H}_7\text{O}_4\text{N}\cdot\text{H}_2\text{O}$ , prepared by the oxidation of the above amino- $\alpha$ -naphthaquinolines with dilute potassium permanganate in dilute sulphuric acid solution cooled by ice, crystallises in stellate aggregates of microscopic prisms, melts and decomposes at  $206\text{--}207^\circ$ , and yields an odour of quinoline when sublimed. The *hydrochloride* crystallises in long prisms and melts and decomposes at  $212^\circ$ ; the *sodium hydrogen* ( $+3\text{H}_2\text{O}$ ), *acid copper*, *normal copper* ( $+ \frac{1}{2}\text{H}_2\text{O}$ ), *nickel*, *lead*, and *silver* salts are described.

The amine melting at  $175^\circ$  yields on oxidation, together with quinoline-7 : 8-dicarboxylic acid, an amorphous product which is probably  $\alpha$ -phenylpyridinedicarboxylic acid.

G. Y.

**Quinonaphthalone.** ALEXANDER EIBNER and M. LÖBERING (*Ber.*, 1906, 39, 2215—2218. Compare Eibner, *Abstr.*, 1904, i, 1049).—*s*-Quinonaphthalone,  $\text{C}_{22}\text{H}_{13}\text{O}_2\text{N}$ , prepared by heating 1 : 8-naphthalic anhydride with 2-methylquinoline and zinc chloride at  $210^\circ$ , forms long, matted, greenish-yellow needles, melts at  $261^\circ$ , is readily soluble in chloroform or glacial acetic acid, and forms traces of an unstable, dark red compound with aniline. The *sodium* derivative,  $\text{C}_{22}\text{H}_{12}\text{O}_2\text{NNa}$ , crystallises from alcohol in sheaves of yellowish-red needles and is decomposed by dilute mineral acids or much water. The action of bromine on quinonaphthalone in chloroform solution at  $50\text{--}60^\circ$  leads

to the formation of a *perbromide*,  $C_{22}H_{12}O_2NBr_4$ , which crystallises in small, glistening, orange-yellow leaflets, melts and loses bromine at  $239^\circ$ , decomposes when recrystallised from chloroform, and yields quinonaphthalone when treated with alcohol, water, or ammonia. The *perbromide*,  $C_{22}H_{12}O_2NBr_6$ , formed by the action of an excess of bromine on quinonaphthalone in cold chloroform solution, crystallises in long, matted, yellowish-brown needles, and when heated with water yields a *monobromo-derivative*, which crystallises in white leaflets, becomes yellow, and yields quinonaphthalone when recrystallised (compare Eibner and Merkel, Abstr., 1902, i, 494).

*as-Quinonaphthaline*,  $C_{22}H_{14}ON_2$ , prepared by heating naphthalimide with 2-methylquinoline and zinc chloride at  $180^\circ$ , crystallises in long, orange-red needles, melts at  $235^\circ$ , is only sparingly soluble in alcohol, ether, or light petroleum, and with bromine in chloroform solution forms a *bromo-derivative*, which crystallises in light brown needles and forms a blood-red precipitate with diazonium chloride in sodium hydroxide solution.

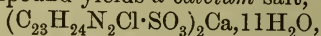
*as-Quinonaphthalone*, *as-quinophthaline*, and *as-quinonaphthaline* decolorise potassium permanganate rapidly in cold acetone solution, whereas *s-quinophthalone* and *s-quinonaphthalone* give a red coloration with potassium permanganate, which is decolorised only on prolonged heating. The action of the *s-* as also of the *as-* compounds on potassium permanganate is accelerated by the presence of sodium carbonate. G. Y.

**Influence of Nuclear Substituents on the Shade of Malachite-green.** EMILIO NOELTING and PAUL GERLINGER (*Ber.*, 1906, 39, 2041—2053).—E. and O. Fischer have already shown that a nitro-substituent in the para-position produces a yellower shade of green, but in the ortho-position a bluer shade, and that it is practically without effect in the meta-position. Similar generalisations hold good with respect to methyl, chlorine, and methoxyl, chlorine producing the greatest effect and methoxyl the least. *p'p''-Tetramethyldiamino-o'''-methyltriphenylmethane*,  $C_6H_5Me \cdot CH(C_6H_5 \cdot NMe_2)_2$ , is most readily prepared (95 per cent. yield) by condensing *o*-tolualdehyde with dimethylaniline, and may also be obtained, although not in a crystalline form, by eliminating the amino-group from the condensation product of Michler's hydrol and *m*-toluidine, or by the action of phosphorus oxychloride on *o*-toluic acid and dimethylaniline. It crystallises from alcohol in glistening needles, melts at  $102\text{--}103^\circ$ , and when oxidised with lead peroxide and hydrochloric acid yields a dye, the *additive* compound of which, with zinc chloride, forms green crystals with a bronze lustre and yields blue solutions. The sulphonic acid of the leuco-compound yields a *barium* salt,  $(C_{24}H_{27}O_3N_2S)_2Ba \cdot 8H_2O$ , in the form of soft, glistening plates, which readily turn green on exposure to the air.

The corresponding *p'p''-tetramethyldiamino-m'''-methyltriphenylmethane*, obtained from *m*-tolualdehyde, crystallises from alcohol in colourless needles and melts at  $84\text{--}85^\circ$ . When oxidised, it yields a copper-red dye, but the aqueous solutions are bluish-green and so impart a blue colour to fabrics. The *p'''-methyl* derivative (Hanzlik and Bianchi,



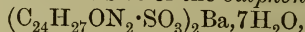
Abstr., 1899, i, 597) yields an oxidation product which dyes yellowish-green. The leuco-compound yields a *sulphonic acid*, the *sodium* salt of which,  $C_{24}H_{27}N_2 \cdot SO_3Na \cdot 2\frac{1}{2}H_2O$ , when oxidised yields a dye which imparts the same colour to a fabric as the non-sulphonated dye. The 2 : 3 : 6-trimethyl derivative,  $C_6H_2Me_3 \cdot CH(C_6H_4 \cdot NMe_2)_2$ , prepared by eliminating the amino-group from aminotetramethyldiaminotriphenylmethane (Abstr., 1892, 187), has not been obtained in a crystalline form. When oxidised it yields a dark red dye which dissolves in water to a blue solution. *o'''*-Chloro-*p'''*-tetramethyldiaminotriphenylmethane crystallises from alcohol or toluene in glistening needles, melts at 145—146°, and on oxidation yields Geigy's setocyanin. The zincochloride dyes a greenish-blue. The *sulphonic acid* of the leuco-compound yields a *calcium* salt,



which crystallises from water in glistening needles. When oxidised it yields a product which dyes blue.

The *m'''*-chloro-derivative, when crystallised from alcohol mixed with a little zinc dust, forms colourless needles, melts at 112°, and dissolves readily in most organic solvents. The *p'''*-chloro-derivative melts at 98—99°, and not at 142—143° as stated by Kaeswurm (Abstr., 1886, 552).

*p'''*-Tetramethyldiamino-*o'''*-methoxytriphenylmethane, obtained by condensing dimethylaniline and the methyl ether of salicylaldehyde with alcoholic hydrochloric acid, crystallises from alcohol in glistening needles, melts at 146°, and is only sparingly soluble in ether. The *sodium* salt of the *sulphonic acid* crystallises in glistening plates, and the *ammonium* salt,  $C_{24}H_{27}ON_2 \cdot SO_3NH_4 \cdot H_2O$ , in slender needles. The *m'''*-methoxy*leucomalachite-green* forms glistening plates melting at 123° and is fairly readily soluble in alcohol or ether. The isomeric *p'''*-methoxy-compound melts at 105° and dissolves readily in most organic solvents. The *barium* salt of the *sulphonic acid*,



and the *sodium* salt,  $C_{24}H_{27}ON_2 \cdot SO_3Na \cdot 8H_2O$ , have been analysed.

A small amount of *p'''*-tetramethyldiaminotriphenylmethane-3'''-sulphonic acid has been obtained by oxidising the corresponding sulphonic acid, prepared by the action of sulphur dioxide and copper powder on diazotised *m'''*-aminoleucomalachite-green. When oxidised it yields a green dye similar to malachite-green.

J. J. S.

**Derivatives of 3-Hydroxy-1-phenyl-5-pyrazolone.** MAX CONRAD and A. ZART (*Ber.*, 1906, 39, 2282—2288. Compare Michaelis and Burmeister, Abstr., 1892, 1004; 1899, i, 233).—3-Hydroxy-1-phenyl-5-pyrazolone can be prepared directly, in 64 per cent. yield from sodium, ethyl malonate, and phenylhydrazine in alcoholic solution; after removal of the alcohol, the residue is heated at 110—120° for twelve hours, cooled, dissolved in water, and, after extraction with ether, the aqueous portion is acidified and the precipitate recrystallised.

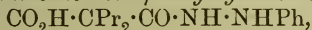
4-Amino-3-hydroxy-1-phenyl-5-pyrazolone, obtained by reducing the nitroso-compound (Michaelis, *loc. cit.*) with ammonium sulphide at 30—40°, is a yellow substance which decomposes at 320° and is insoluble in acids.

3-Hydroxy-1-phenyl-4:4-diethyl-5-pyrazolone, obtained as above from ethyl diethylmalonate, crystallises in long, prismatic needles, melts at 114—115°, and can be heated in alkaline solution for a long time without decomposition.

3-Methoxy-1-phenyl-4:4-diethyl-5-pyrazolone, obtained from an alkaline solution of the preceding compound and methyl sulphate, forms pearly leaflets, melts at 94—95°, and is soluble after long boiling in aqueous solutions of alkali hydroxides, from which sulphuric acid precipitates the unchanged substance in crystals containing 2H<sub>2</sub>O and melting completely at 166°. Of the 2H<sub>2</sub>O, 1 mol. is water of crystallisation, the other of constitution. Sodium hydroxide neither hydrolyses the compound nor breaks the ring (compare Michaelis (*loc. cit.*)).

3-Acetoxy-1-phenyl-4:4-diethyl-5-pyrazolone melts at 97°, and the corresponding benzoyl derivative at 110°.

3-Hydroxy-1-phenyl-4:4-dipropyl-5-pyrazolone, obtained in similar manner to the diethyl compound, forms short prisms and melts at 103—105°; dipropylmalonic acid phenylhydrazide,



which occurs as a by-product, melts at 148° evolving carbon dioxide.

3-Hydroxy-1-phenyl-5-pyrazolonimide,  $\begin{array}{c} \text{N} \cdot \text{NPh} \\ | \quad | \\ \text{OH} \cdot \text{C} \cdot \text{CH}_2 \end{array} > \text{C} : \text{NH}$ , obtained from sodium ethoxide, phenylhydrazine, and ethyl cyanoacetate, crystallises in prisms, melts at 219°, and is soluble in mineral acids or in alkalis. By treatment with sodium nitrite and dilute acetic acid, a quantitative yield of the isonitroso-compound is obtained, which melts and decomposes at 223°.

3-Hydroxy-1-phenyl-4:4-diethyl-5-pyrazolonimide, obtained from ethyl cyanodiethylacetate, separates from hot water in crystals containing 2H<sub>2</sub>O, melts at 211—213°, and is not changed by boiling dilute mineral acids. C. S.

**Oxidation of Naphthaphenazine by Chromic Acid.** II. OTTO FISCHER and ERICH SCHINDLER (*Ber.*, 1906, 39, 2238—2244. Compare *Abstr.*, 1904, i, 111).—A convenient method of preparing diketonaphthaphenazine by the oxidation of naphthaphenazine by chromic acid is described.



is one of the products obtained by boiling diketonaphthaphenazine with a concentrated aqueous solution of sodium hydroxide; crystallises in silvery, flat prisms or leaflets, is easily soluble in hot water, and melts at 237°, water being eliminated and the stable lactone formed. Its solution in concentrated sulphuric acid is yellow. Its barium salt forms silky needles. Its lactone, C<sub>15</sub>H<sub>8</sub>O<sub>2</sub>N<sub>2</sub>, formed by heating the acid either alone or with glacial acetic acid or acetic anhydride, exhibits dimorphism, separating from benzene or acetone in prisms, which are gradually transformed into hexagonal crystals; it melts at 207—208°.

The lactone may also be formed directly from diketonaphthaphenazine by oxidising it, under the conditions described, with chromic

acid. *Ketoindenephenazine*,  $C_6H_4 \begin{smallmatrix} N \cdot C & \text{---} & C \cdot CH \cdot CH \\ | & & | \\ N \cdot C & \cdot CO \cdot & C \cdot CH \cdot CH \end{smallmatrix}$ , formed as a by-product in the preceding reaction, separates from glacial acetic acid in yellow prisms and melts at  $187^\circ$ . It forms a brownish-red solution with concentrated sulphuric acid. Its *phenylhydrazone* separates from alcohol in red needles and melts at  $216\text{--}217^\circ$ .

*Phenylquinoxalinecarboxylic acid*,  $C_6H_4 \begin{smallmatrix} N \cdot C \cdot C_6H_4 \cdot CO_2H \\ | \\ N \cdot CH \end{smallmatrix}$ , obtained by fusing diketonaphthaphenazine with sodium hydroxide until vapours are evolved, differs from hydroxyphenylquinoxalinecarboxylic acid in being sparingly soluble in water. It melts and decomposes at about  $275^\circ$ , and forms a yellow solution with concentrated sulphuric acid. It is a weak acid. When distilled, it loses carbon dioxide and is transformed into phenylquinoxaline. A. McK.

*o*-Hydroxytriphenylmethane Derivatives. EMILIO NOELTING and PAUL GERLINGER (*Ber.*, 1906, 39, 2053—2056).—p'p'p'''-Hexamethyl-triamino-o'''-hydroxytriphenylmethane,

$NMe_2 \cdot C_6H_3(OH) \cdot CH(C_6H_4 \cdot NMe_2)_2$ , obtained by condensing dimethyl-*m*-aminophenol with Michler's hydrol in an alcoholic solution of hydrogen chloride, crystallises from alcohol in colourless needles and melts and decomposes at  $172\text{--}174^\circ$ . It turns red in contact with the air and dissolves readily in most organic solvents, but is not readily oxidised to a dye owing to the presence of the *o*-hydroxy-group. The *acetyl* derivative,  $C_{25}H_{30}ON_3Ac$ , crystallises from alcohol mixed with a small amount of zinc dust in colourless needles melting at  $171\text{--}173^\circ$ . It changes colour more readily than the original hydroxy-compound on exposure to the air, and is readily oxidised by lead peroxide to the corresponding dye; the *additive* compound of the chloride with zinc chloride forms a dark violet powder which dyes fabrics purple-blue. The *picrate* is sparingly soluble.

p'p'p'''-Hexamethyltriamino-o'o''-dihydroxytriphenylmethane,  $NMe_2 \cdot C_6H_4 \cdot CH[C_6H_3(OH) \cdot NMe_2]_2$ , obtained by condensing dimethyl-*m*-aminophenol with dimethyl-*p*-aminobenzaldehyde in alcoholic hydrogen chloride, crystallises from dilute alcohol in colourless needles melting and decomposing at  $175^\circ$ . It gradually turns red on exposure to the air, and dissolves readily in organic solvents and in alkalis. The hydroxylic compound is not readily oxidised, but with acetic acid and lead peroxide yields a bluish-red dichroic solution which gives a violet-blue colour when diluted. The *diacetyl* derivative,  $C_{25}H_{29}O_2N_3Ac_2$ , forms a pale red mass which does not crystallise. On exposure to the air, it gradually turns blue, and can be oxidised readily to a dye, the chloride of which forms a violet powder with zinc chloride.

When the dihydroxy-derivative is warmed with concentrated sulphuric acid on the water-bath, it yields the non-crystalline *anhydro-leuco-compound*,  $NMe_2 \cdot C_6H_3 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH(C_6H_4 \cdot NMe_2) \end{smallmatrix} C_6H_3 \cdot NMe_2$ , which is readily oxidised to a dye when heated at  $140^\circ$  with concentrated sulphuric acid. The dye base is dark red and the salts dark green, but



produce a violet colour on the fabric. Solutions in mineral acids have an intense reddish-yellow colour and are strongly fluorescent. The compound is a dimethyl-*p*-amino-derivative of rosamine. J. J. S.

**Constitution of Murexide and of Purpuric Acid.** RICHARD MÖHLAU and HANS LITTER (*J. pr. Chem.*, 1906, [ii], 73, 449—472. Compare Möhlau, *Abstr.*, 1904, i, 654; Slimmer and Stieglitz, *Abstr.*, 1904, i, 634; Piloty and Finckh, *ibid.*, 820).—The authors consider that the formulæ  $\text{CO} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CO}$  for purpuric acid and  $\text{CO} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{O} \cdot \text{NH}_4) \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CO}$  for murexide are in accordance with the following facts:

The action of alloxan on ethyluramil in presence of ammonium carbonate leads to the formation of murexide and alcohol.

Alkylpurpuric acids cannot be prepared by oxidation of dibarbituryl-alkylamines. Alkylamine purpurates are formed by the action of alkylamines on alloxan and alloxantin, or of alkylamine carbonates and acetates on alloxan. The reddish-orange purpuric acid is unstable towards water. The formation of an unstable methyl purpurate by the action of methyl iodide on silver purpurate (Slimmer and Stieglitz, *loc. cit.*) is confirmed.

The relation of the constitution of murexide to its dyeing properties is discussed.

The hydrolysis of murexide by boiling water, or by cold or boiling dilute hydrochloric acid, leads to the formation on the one hand of uramil and alloxan, and on the other of alloxantin. As these products are further hydrolysed by prolonged boiling with water, their amounts are at any time a function of the duration of the hydrolysis.

*Methylamine purpurate*,  $\text{C}_9\text{H}_{10}\text{O}_6\text{N}_6 \cdot \text{H}_2\text{O}$ , forms red, microscopic, rhombic crystals, or large, green, shimmering rhomboids, loses  $\text{H}_2\text{O}$  at  $110^\circ$ , decomposes at  $210^\circ$ , and when heated with water yields 7-methyluramil, alloxantin, alloxan, and methylamine.

*Ethylamine purpurate*,  $\text{C}_{10}\text{H}_{12}\text{O}_6\text{N}_6 \cdot \text{H}_2\text{O}$ , forms red prisms, decomposes about  $205^\circ$ , and when heated with water yields alloxan, ethylamine, traces of alloxantin, and 7-ethyluramil,  $\text{C}_6\text{H}_9\text{O}_3\text{N}_3$ , which crystallises in hexagonal prisms.

*p*-Hydroxyphenylmisesatine,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , prepared by boiling isatin with *p*-aminophenol hydrochloride in alcoholic solution in presence of sodium acetate, crystallises in red prisms, melts above  $300^\circ$ , is insoluble in water or benzene, but is sparingly soluble in toluene, chloroform, methyl alcohol, or ethyl acetate, and is readily so in pyridine; it dissolves in aqueous alkali hydroxides forming a red, in concentrated sulphuric acid forming a reddish-brown solution, and is hydrolysed by boiling dilute acids, forming isatin and *p*-aminophenol.

*p*-Dimethylaminophenylmisesatine,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , prepared from isatin and dimethyl-*p*-aminoaniline, crystallises in glistening, metallic leaflets and melts at  $215^\circ$ .

*p*-Aminophenylmesatine,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C:N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , crystallises in reddish-brown needles and melts above  $300^\circ$ . G. Y.

**Action of Primary Amines on Alloxantin.** RICHARD MÖHLAU and HANS LITTER (*J. pr. Chem.*, 1906, [ii], 73, 472—487. Compare Möhlau, *Abstr.*, 1904, i, 654).—Dibarbiturylalkylamines, prepared together with alloxan by boiling alloxantin, or alone by boiling dialuric acid with the hydrochlorides of primary amines in aqueous solution (Möhlau, *loc. cit.*), are colourless, crystalline, dibasic acids, dissolve in dilute alkali carbonates or hydroxides, and are hydrolysed by boiling aqueous alkali hydroxides, forming dialuric acid and the amine.

Dibarbiturylmethylamine (*loc. cit.*), which is formed also by the action of dialuric acid on 7-methyluramil, decomposes at  $280^\circ$  and reddens blue litmus solution. The *sodium* salt,  $\text{C}_9\text{H}_7\text{O}_6\text{N}_5\text{Na}_2$ , crystallises from alcohol.

Dibarbiturylethylamine,  $\text{NEt}(\text{C}_4\text{H}_3\text{O}_3\text{N}_2)_2$ , forms rhombic crystals, becomes red at  $235^\circ$ , but is not completely decomposed at  $300^\circ$ , and in aqueous solution has an acid reaction. The *sodium* salt,  $\text{C}_{10}\text{H}_9\text{O}_6\text{N}_5\text{Na}_2$ , crystallises in needles.

Dibarbiturylphenylamine,  $\text{NPh}(\text{C}_4\text{H}_3\text{O}_3\text{N}_2)_2$ , crystallises in white needles, becomes blue at  $240^\circ$ , and is oxidised superficially, becoming green on exposure to air.

Dibarbituryl- $\alpha$ -naphthylamine,  $\text{C}_{10}\text{H}_7\text{N}(\text{C}_4\text{H}_3\text{O}_3\text{N}_2)_2$ , becomes black at  $260^\circ$  and forms a *sodium* salt,  $\text{C}_{18}\text{H}_{11}\text{O}_6\text{N}_5\text{Na}_2$ , which crystallises in glistening leaflets.

Dibarbituryl- $\beta$ -naphthylamine crystallises in colourless needles, decomposes at  $260^\circ$ , and is insoluble in indifferent solvents. The *sodium* salt,  $\text{C}_{18}\text{H}_{11}\text{O}_6\text{N}_5\text{Na}_2$ , crystallises in large leaflets.

The action of benzylamine on alloxantin leads to the formation of benzyluramil,  $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_4\text{H}_3\text{O}_3\text{N}_2$ , which crystallises from hot glacial acetic acid in needles, decomposes at about  $280^\circ$ , and has feeble basic properties, crystallising from its solution in concentrated hydrochloric acid on cooling, but forms a *sodium* salt,  $\text{C}_{11}\text{H}_9\text{O}_3\text{N}_3\text{Na}_2$ ; this crystallises in tetragonal prisms. When heated with aqueous sodium hydroxide, the uramil is slowly hydrolysed, forming benzylamine.

Phenylethyluramil,  $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{O}_3\text{N}_2$ , formed by the action of  $\beta$ -phenylethylamine on alloxantin, crystallises in prisms, melts above  $300^\circ$ , is readily soluble in aqueous sodium carbonate, has feeble basic properties, and is hydrolysed by boiling sodium hydroxide, forming phenylethylamine and dialuric acid.

Dibarbiturylcarbamide,  $\text{CO}(\text{NH} \cdot \text{C}_4\text{H}_3\text{O}_3\text{N}_2)_2$ , is formed by boiling alloxantin with carbamide and hydrochloric acid in aqueous solution in a reflux apparatus; it crystallises in spears, decomposes above  $300^\circ$ , and is readily soluble in aqueous sodium carbonate or alkali hydroxides, forming solutions which evolve ammonia when boiled.

Alloxazine (Kühling, *Abstr.*, 1891, 1341), prepared from alloxantin and *o*-phenylenediamine hydrochloride, forms a greyish-green powder and decomposes above  $300^\circ$ . The *sodium* salt,  $\text{C}_{10}\text{H}_4\text{O}_2\text{N}_4\text{Na}_2$ , crystallises in yellow needles.

Alloxantin and *m*-phenylenediamine hydrochloride interact, forming a dark brown to black, amorphous *precipitate*.

*Bisanhydroalloxan-p-phenylenediamine*,  $C_6H_4(N:C_4H_3O_3N_2)_2$ , prepared from alloxantin and *p*-phenylenediamine hydrochloride, forms blue needles with green lustre, melts above  $300^\circ$ , and dissolves in concentrated sulphuric acid or aqueous alkali hydroxides or carbonates, forming a bluish-violet solution. When boiled with an aqueous alkali hydroxide, it is hydrolysed to the diamine and alloxan, the solution becoming colourless, but as the solution cools the anhydro-compound is re-formed.

*Dibarbituryl-p-phenylenediamine*,  $C_{14}H_{12}O_6N_6$ , is formed by the action of dialuric acid on *p*-phenylenediamine hydrochloride; it crystallises in colourless prisms, is readily soluble in aqueous sodium carbonate or hydroxide, and when boiled with alloxan in aqueous solution is oxidised slowly, in ammoniacal solution more rapidly, yielding bisanhydro-alloxan-*p*-phenylenediamine.

*Dibarbituryl-2:5-tolylenediamine*,  $C_6H_3Me(NH \cdot C_4H_3O_3N_2)_2$ , prepared from alloxantin and tolylene-2:5-diamine hydrochloride, forms colourless crystals, melts above  $300^\circ$ , is readily soluble in aqueous sodium hydroxide or carbonate or concentrated hydrochloric acid, and when oxidised with potassium permanganate in hot dilute sulphuric acid solution yields a blue, flocculent *product* (*bisanhydroalloxan-2:5-tolylenediamine*?).

*Dibarbiturylbenzidine*,  $C_{12}H_8(NH \cdot C_4H_3O_3N_2)_2$ , prepared from alloxantin and benzidine hydrochloride, is obtained as a greyish-white, amorphous, flocculent substance, and is not hydrolysed by boiling aqueous sodium hydroxide; the *sodium* salt,  $C_{20}H_{14}O_6N_6Na_2$ , crystallises in colourless needles. G. Y.

**Mixed Azo-compounds. II.** ALEXANDER EIBNER and O. LAUE (*Ber.*, 1906, 39, 2022—2027).—1-Phenyl-3-methylpyrazoloneazobenzene (*Abstr.*, 1903, i, 871) reacts with a chloroform solution of bromine, yielding dark reddish-brown crystals of the perbromide,  $C_{16}H_{12}ON_4Br_6$ , which with ammonia yields *dibromophenylmethylpyrazoloneazobenzene*,  $C_{16}H_{12}ON_4Br_2$ . This crystallises from a mixture of ether and chloroform in slender, orange-red needles and melts at  $227^\circ$ .

With sodium hydroxide or, better, sodium ethoxide, it yields a crystalline *sodium* derivative,  $C_{16}H_{11}ON_4Br_2Na$ , and when reduced with tin and hydrochloric acid it yields dibromorubazonic acid, melting at above  $300^\circ$ , and *p*-bromoaniline. It has not been found possible to couple mono-substituted pyrazolone derivatives which contain the substituent in the methylene group with diazobenzene.

Phenylhydrazineketopyrazolonecarboxylic acid does not yield a perbromide, but simply a mono-substituted derivative,  $C_{10}H_{11}O_3N_4Br$ , which crystallises from glacial acetic acid in golden-yellow needles and melts at  $258^\circ$ .

Phenylhydrazineketopyrazolone dissolves in sodium hydroxide solution, and with a chloroform solution of bromine yields a *perbromide*,  $C_{15}H_{11}ON_4Br_3$ . This crystallises in dark reddish-brown prisms and reacts with alkali, yielding compact crystals of a *bromo-derivative*,



$C_{15}H_{11}ON_4Br$ , melting at  $224^\circ$ . When reduced with zinc dust and acetic acid, the carboxylic acid yields aniline and rubazonecarboxylic acid (Bernthsen, *Chem. Zeit.*, 1898, 457). The monobromo-derivative yields *p*-bromoaniline and rubazonecarboxylic acid.

These reactions indicate that the acid is an azo-compound, namely, the carboxylic acid of ketophenylpyrazoloneazobenzene. The views of Bernthsen and R. Meyer regarding the structure of tartrazin are thus confirmed.

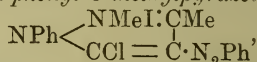
Ketophenylpyrazoloneazocarboxylic acid yields a *disodium* derivative,  $C_{16}H_{10}O_3N_4Na_2$ , in the form of golden-yellow crystals which are readily hydrolysed by water to the monosodium salt. *cyclo*Pentadieneazobenzene also forms a *perbromide*. J. J. S.

**Benzeneazo-derivatives of Antipyrine and Thiopyrine.** AUGUST MICHAELIS and H. SCHLECHT (*Ber.*, 1906, 39, 1954—1956).—

4-Benzeneazoantipyrine,  $NPh \begin{matrix} \text{NMe:CMe} \\ >O | \\ C=C \cdot N_2Ph \end{matrix}$ , is formed by heating

4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone with methyl sulphate; it crystallises in reddish-yellow leaflets, melts at  $174^\circ$ , is readily soluble in alcohol or in hydrochloric acid, forming a deep red solution, and is insoluble in aqueous sodium hydroxide.

4-Benzeneazo-5-chloro-1-phenyl-3-methylpyrazole methiodide,



is prepared by treating 4-benzeneazo-5-chloro-1-phenyl-3-methylpyrazole (Michaelis and Leonhardt, *Abstr.*, 1904, i, 124) with an excess of methyl sulphate, neutralising the product with sodium carbonate, and adding a concentrated solution of potassium iodide; it crystallises in slender, yellow needles and melts at  $170^\circ$ . The *methochloride*, prepared by boiling the methiodide with silver chloride in aqueous-alcoholic solution, forms reddish-yellow crystals and melts at  $164^\circ$ .

When treated with potassium hydrogen sulphide in aqueous solution,

the methiodide yields 4-benzeneazothiopyrine,  $NPh \begin{matrix} \text{NMe:CMe} \\ >S | \\ C=C \cdot N_2Ph \end{matrix}$ ,

which forms stout, dark red crystals, melts at  $216^\circ$ , is readily soluble in alcohol, and with acids forms unstable, dark red salts (compare Michaelis, Leonhardt, and Wahle, *Abstr.*, 1905, i, 392). G. Y.

**The Rendering Insoluble of Gelatin during Photographic Development, particularly by the Use of Pyrogallol Developers.** AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 377—381. Compare *Abstr.*, 1905, i, 847, 848).—The results of experiments with a number of developers show that gelatin only becomes insoluble when the developers are in presence of alkali and in contact with air, and that probably the active agents in rendering the gelatin insoluble are the oxidation products formed from the developers. Where the oxidation product is insoluble in dilute alkalis, as in the case of *p*-aminophenol, the action is slight. The action is usually most marked

in the neighbourhood of the reduced silver, and this is probably due to the more rapid oxidation of the developer in that region by the bromine liberated.

T. A. H.

**Action of Ozone and other Oxidising Agents on Lipase.** JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1555—1556; from *Public Health and Marine-Hospital Service of the U.S. Hygienic Lab. Bull.* No. 26, 37—41).—The activity of a quantity of lipase from pig's liver which was found capable of hydrolysing 0.058 gram of ethyl butyrate in four and a quarter hours was destroyed by the action of 1.009 mg. of ozone in forty minutes. When a second quantity of lipase, which under normal conditions hydrolysed 0.058 gram of ethyl butyrate in twenty-four hours, was treated with 0.312 mg. of ozone, its hydrolytic action sank to 0.00116 gram in twenty-four hours.

Silver nitrate, hydriodic acid, formaldehyde, cresols, hydrocyanic acid, potassium nitrate, and succinic acid had practically no poisonous action on lipase; mercuric chloride, chromic acid, copper sulphate, and perosmic acid were moderately poisonous; ozone, chlorine, bromine, sodium fluoride, cyanogen iodide, and potassium permanganate were strongly poisonous. The poisonous effect of cyanogen iodide increased with rise of temperature.

E. W. W.

**Stability of Oxydases and their Behaviour towards Various Reagents.** JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1554—1555; from *Public Health and Marine-Hospital Service of the U.S. Hygienic Lab. Bull.* No. 26, 7—22).—The oxydase of *Sepiota americana* retains its activity for weeks or months and appears to be more stable in glycerol than in water. The presence of oxydases has been detected in the aqueous and glycerol extracts of a number of moulds indigenous to Columbia, but not in the extracts of the very poisonous *Amanita verna*. Whilst the oxidising action of the glycerol extracts of *Lactarius piperatus*, *Lactarius volumen*, and *Lactarius indigo* did not decrease in four months, in other cases, for instance, in that of *Volvaria bombycina*, the activity of the extract rapidly diminished. The oxydases are less stable in water than in glycerol and are not so rapidly destroyed by toluene as by chloroform or thymol. The oxydases of *Lepiota americana* are precipitated from the aqueous solution by alcohol in a colloidal form. An aqueous solution of material which had been dried in the air and exposed for four and a half months gave a strong blue coloration with guaiacum tincture. The oxidising power of the substance is destroyed at 80—90°, but it withstands heating for a short time at 30°. When the fresh mould is kept for some time in an atmosphere of hydrogen, reducing substances are formed which decolorise guaiacum-blue; the formation of these compounds may be due to anaërobic bacteria or to the mould itself. The oxydase is more readily soluble in water than in other solvents, and is not destroyed by a 40 per cent. solution of formaldehyde; it is insoluble in ethyl or amyl alcohol and its activity is not affected. It dissolves in glycerol and apparently to a certain extent in toluene. Certain substances such as chlorine hydrate completely destroy the oxydase.

A deep purple-red coloration is produced when aqueous potato

extract is added to a slightly alkaline solution of leucorosolic acid, but strongly alkaline or acid solutions are scarcely oxidised. The ethyl ester of phenolphthalein gives a similar reaction, but the presence of bromine in the ethyl ester of tetrabromophenolphthalein appears to prevent oxidation by vegetable oxydases; benzoyl peroxide and benzoyl acetyl peroxide oxidise the latter compound, however, forming a bluish-green coloration. An alcoholic solution of aloin gives a red coloration with vegetable oxydases; the sensitiveness of the reagent is considerably increased by shaking with zinc dust, filtering, and exposing to air for a short time, but it loses its property in some days. The red substance which is formed is soluble in water and in the aqueous extracts containing oxydases; it is more stable than the blue compound formed by the oxidation of guaiacum tincture. The sensitiveness of the aloin and guaiacum reactions is about the same. The intensity of the peroxydase reaction of aloin in aqueous extracts of the leaves of *Phytolacca decandra* depends on the concentration of the hydrogen peroxide, but if only small quantities are used there is but little variation. Whilst the peroxydase reaction of extracts of horseradish, potato parings, and other vegetable oxydases is improved by the addition of a small quantity of hydrogen peroxide, larger quantities are required in the case of animal oxydases. E. W. W.

**Peroxydases as Specifically-acting Enzymes.** ALEXIS BACH (*Ber.*, 1906, 39, 2126—2129).—Tyrosine is not oxidised by the system peroxydase—hydrogen peroxide, although the oxidation reactions of ordinary oxydases are effected by this system. The specific action of tyrosinase in oxidising tyrosine is to be ascribed either to the specific nature of its peroxydases or of its oxygenases (since all oxydases are mixtures of peroxydases and oxygenases); the author has accordingly separated, with partial success, the peroxydases of tyrosinase from the oxygenases. Potato juice was used; the fresh juice oxidised tyrosine rapidly, whilst after the treatment with alcohol described, the oxygenases were almost entirely destroyed; the final product contained peroxydases, but had very little oxidising action on tyrosine. On the supposition that the falling off of the tyrosine action was due to the partial destruction of the oxygenases, the latter were replaced by hydrogen peroxide, the addition of which caused the solution to exert an oxidising action on tyrosine.

Similar results were obtained with the mixture of ordinary oxydases and of tyrosinase contained in the juice of *Lactarius velereus*. The specific action of tyrosinase is due to the specific nature of its peroxydases.

Various theoretical considerations are adduced.

A. McK.



## Organic Chemistry.

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**Purification of Acetylene by means of Calcium Hypochlorite.** HUGO DITZ (D.R.-P. 162324).—In the purification of acetylene by means of commercial bleaching powder, spontaneous heating occurs, and explosions may arise from the formation of chlorine and nitrogen chloride. This is avoided by using the definite compound  $\text{CaO}, \text{CaOCl}_2, 2\text{H}_2\text{O}$  or the compound  $\text{CaO}, \text{CaOCl}_2, \text{H}_2\text{O}$ , obtained by heating the former (Abstr., 1901, ii, 239). These substances do not evolve chlorine when heated, but decompose at  $130\text{--}140^\circ$ , evolving oxygen.

C. H. D.

**aci-Esters of Nitroform.** ARTHUR HANTZSCH and K. S. CALDWELL (Ber., 1906, 39, 2472—2478).—*aci*-Methylnitroform has not been obtained, but in the reaction between methyl iodide and silver nitroform a small amount of nitroform is always obtained, the quantity increasing with diminishing temperature; its production is due to the hydrolysis of the *aci*-methyl ester by the water from the hydrated silver nitroform.

Ethereal solutions of hydrated silver nitroform and of methyl iodide react at  $-75^\circ$  with the instantaneous separation of an intensely yellow substance, *aci-silver nitroform di-methyl iodide*,  $\text{C}(\text{NO}_2)_3 \cdot \text{NO} \cdot \text{OAg}, 2\text{MeI}$ , which from the rapidity of its formation is regarded as an additive compound and not as having the constitution  $\text{C}(\text{NO}_2)_3 \cdot \text{NO} \cdot \text{OMe}, \text{AgI}, \text{MeI}$ . The substance is very unstable and decomposes spontaneously at  $6\text{--}8^\circ$  in air or in indifferent anhydrous solvents into silver iodide and trinitroethane, but in the presence of water nitroform is produced quantitatively.

The theoretical importance of these decompositions is discussed.

Benzyl iodide and allyl iodide yield similar additive compounds which are even less stable. Ethyl iodide, which at the ordinary temperature yields trinitropropane, an oil with the odour of nitrous acid, does not react at low temperatures with silver nitroform.

C. S.

**Trinitromethane and Triphenylmethane.** ARTHUR HANTZSCH (Ber., 1906, 39, 2478—2486).—[With K. S. CALDWELL.]—*Iodopicrin*,  $\text{CI}(\text{NO}_2)_3$ , obtained from iodine and silver nitroform, melts and turns brown at  $58^\circ$ , is decomposed by silver nitrate, slowly in the cold, more rapidly on boiling, reacts with potassium hydroxide in accordance with the equation  $3\text{CI}(\text{NO}_2)_3 + 6\text{KOH} = 3\text{C}(\text{NO}_2)_3\text{K} + 2\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O}$ , and with silver nitrite yields tetranitromethane. Hexanitroethane is not obtained in the preceding preparation, or by treatment of iodopicrin with silver nitroform, and the author uses this fact as an argument for regarding Gomberg's triphenylmethyl as hexaphenylethane.

The paper is mainly polemical.

C. S.

**Aliphatic Polynitro-compounds.** JAKOB MEISENHEIMER and M. SCHWARZ (*Ber.*, 1906, 39, 2543—2552).—Trinitroethane and potassium ethoxide react to form the potassium derivative of a substance which was regarded by Hantzsch and Rinckenberger (*Abstr.*, 1899, i, 404) as ethyl *aci*-dinitroethane,  $\text{O:N(OEt)(OK)·CHMe·NO}_2$ , and by Meisenheimer (*Abstr.*, 1903, i, 223) as dinitrodiethyl ether,  $\text{OEt·CH}_2\text{·C(NO}_2)_2\text{·NO·OK}$ .

That the latter view is correct is proved by the following considerations. The substance, after crystallisation from alcohol, has the composition  $\text{C}_4\text{H}_7\text{O}_5\text{N}_2\text{K}$ , forms a bromine derivative,  $\text{C}_4\text{H}_7\text{O}_5\text{N}_2\text{Br}$ , which is a colourless oil boiling at  $103\text{--}104^\circ$  under 13 mm. pressure, and by acidification yields dinitrodiethyl ether,  $\text{C}_4\text{H}_8\text{O}_5\text{N}_2$ , a heavy, colourless oil which boils at  $100^\circ$  under 11 mm. pressure.

The potassium derivative of the corresponding methyl dinitroethyl ether,  $\text{OMe·CH}_2\text{·C(NO}_2)_2\text{·NO·OK}$ , is reduced by tin and hydrochloric acid to methoxyacetic acid,  $\text{OMe·CH}_2\text{·CO}_2\text{H}$ . A reaction similar to the one in question takes place between trinitroethane and potassium cyanide in methyl-alcoholic solution, whereby the potassium salt of *aci*-dinitropropionitrile,  $\text{CN·CH}_2\text{·C(NO}_2)_2\text{·NO·OK}$ , is obtained; it separates from water in glistening, yellow leaflets, and by treatment with aqueous silver nitrate yields the explosive silver salt,  $\text{C}_3\text{H}_2\text{O}_4\text{N}_3\text{Ag}$ , which forms yellow needles. The nitrile,  $\text{CN·CH}_2\text{·CH(NO}_2)_2$ , obtained by acidifying the potassium derivative, is an oil which cannot be distilled without decomposition, but by keeping in a vacuum over sulphuric acid it solidifies to a mass of deliquescent, yellow needles.

Methyl  $\beta\beta$ -dinitropropionate,  $\text{CH(NO}_2)_2\text{·CH}_2\text{·CO}_2\text{Me}$ , is obtained by treating potassium dinitropropionitrile, suspended in methyl alcohol, with hydrogen chloride; the crude ester is dissolved in methyl alcohol, cooled, and slowly treated with 10 per cent. methyl-alcoholic potash, and the potassium derivative,  $\text{C}_4\text{H}_5\text{O}_6\text{N}_2\text{K}$ , which separates as an amorphous precipitate, is crystallised from water and methyl alcohol and acidified, when the pure methyl ester is obtained as a colourless oil. Dinitropropionitrile is hydrolysed by concentrated hydrochloric acid, forming dinitropropionic acid, a viscous, green oil, which explodes when heated; the potassium salt is precipitated from alcoholic solution as a yellow, flocculent precipitate.

By treatment with 10 per cent. hydrogen peroxide, potassium dinitropropionitrile yields cyanoacetic acid, which was identified by its conversion into malonic acid. When a methyl-alcoholic solution of trinitroethane is treated with an alkaline solution of hydroxylamine, a quantitative yield of potassium *aci*-dinitroethane is obtained. Iodotrinitromethane,  $\text{CI(NO}_2)_3$ , obtained from iodine and silver nitroform in ethereal solution, forms yellow leaflets, melts at  $55\text{--}56^\circ$ , distils and slightly decomposes at  $48\text{--}48.5^\circ$  under 13 mm. pressure, and undergoes decomposition when quickly heated (compare preceding abstract).

C. S.

**Some Synthetical Reactions of Pinacolin.** LOUIS HENRY (*Compt. rend.*, 1906, 143, 20—22).—Pinacolin reacts with magnesium methyl bromide to form pentamethylethanol in the form of its crystalline hydrate,  $\text{CMe}_3\text{·CMe}_2\text{·OH, H}_2\text{O}$  (compare Butleroff, this Journal,

1875, 1248), which can also be prepared from acetone by the action of magnesium *ter*-butyl chloride. Pinacolin combines with anhydrous hydrogen cyanide, or with a 25 per cent. solution of the acid, to form  $\beta$ -cyano- $\gamma\gamma$ -dimethylbutan- $\beta$ -ol,  $\text{CMe}_3 \cdot \text{CMe}(\text{OH}) \cdot \text{CN}$  (compare Carlinfanti, Abstr., 1898, i, 234; 1899, i, 671), which crystallises in white needles, melts at  $94^\circ$  (Carlinfanti found  $82-87^\circ$ ), is insoluble in water, and very soluble in ether, alcohol, light petroleum, or glacial acetic acid; the *acetyl* derivative,  $\text{CMe}_3 \cdot \text{CMe}(\text{OAc}) \cdot \text{CN}$ , is a pale yellow, slightly viscous liquid, possessing a peculiar sour-sweet odour; it boils at  $228-230^\circ$  under 770 mm. pressure, has a sp. gr. 0.9535 at  $20^\circ$ , and  $n_D$  1.43091.

M. A. W.

**Preparation of Pinacone.** ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1906, 25, 206—207).—A modification of Couturier and Meunier's method for the preparation of pinacone (Abstr., 1905, i, 326). When a solution of 20 grams of mercuric chloride in 200 grams of dry acetone is allowed to drop slowly on to 20 grams of bright magnesium wire in a reflux apparatus, a violent action occurs and the acetone boils; the reaction is completed by heating the contents of the flask until all the acetone has disappeared; this requires from one to two hours; water is then added and the pinacone separated from the mixture by distillation; the yield is 70 grams.

M. A. W.

**Preparation of the Chlorohydrin, the Oxide, and an Unsaturated Alcohol from Normal Diprimary Decylene Glycol [Decan-*ak*-diol].** LEO ALBERTI and BRONISLAV SMIECIUSZEWSKI (*Monatsh.*, 1906, 27, 411—419. Compare Scheuble, Abstr., 1904, i, 1).—The *chlorohydrin*,  $\text{CH}_2\text{Cl} \cdot [\text{CH}_2]_8 \cdot \text{CH}_2 \cdot \text{OH}$ , prepared by heating decylene glycol with hydrochloric acid of sp. gr. 1.19 in a reflux apparatus on the water-bath, is obtained as a strongly refracting, colourless oil which boils at  $164-165^\circ$  under 20 mm. pressure, and is readily soluble in ether, alcohol, benzene, or light petroleum. When heated with powdered, freshly fused sodium hydroxide, the chlorohydrin yields a mixture of the corresponding oxide and an unsaturated alcohol.

*Decamethylene oxide*,  $\text{C}_{10}\text{H}_{20}\text{O}$ , is obtained as a transparent liquid which boils at  $181^\circ$ , does not form an additive compound with bromine, and is not acted on by zinc ethyl at  $180^\circ$ , or by water at  $200^\circ$ , but yields the chlorohydrin when heated with concentrated hydrochloric acid at  $110^\circ$ .

The *unsaturated alcohol*,  $\text{C}_{10}\text{H}_{20}\text{O}$ , boils at  $234-238^\circ$ , and when heated with acetic anhydride and sodium acetate at  $130^\circ$  forms an acetate,  $\text{C}_{12}\text{H}_{22}\text{O}_2$ , which boils at  $242-246^\circ$  and forms an additive compound with 1 mol. of bromine.

G. Y.

**$\alpha\beta\beta$ -Trichloroethyl Ether.** II. GIUSEPPE ODDO and EFISIO AMELI (*Gazzetta*, 1906, 36, i, 480—490. Compare Abstr., 1904, i, 10).—The action on  $\alpha\beta\beta$ -trichloroethyl ether of an aqueous solution of potassium hydroxide or ethylamine or sodium hydrogen sulphite yields the same products as, but proceeds more rapidly than, the action of water.



The first phases of the action of dry ammonia on  $\alpha\beta$ -trichloroethyl ether proceed according to the equations: (1)  $\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt} + 2\text{NH}_3 = \text{CHCl}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{OEt} + \text{NH}_4\text{Cl}$ ; (2)  $2\text{CHCl}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{OEt} = \text{CHCl}_2 \cdot \text{CH}(\text{OEt})_2 + \text{CHCl}_2 \cdot \text{CH}(\text{NH}_2)_2$ . The last compound is, however, unstable, and gives rise to resinous, complex nitrogen compounds of basic character.

Powdered magnesium has little action on  $\alpha\beta$ -trichloroethyl ether, either by itself or in presence of a solvent. When benzene is used as solvent and the mixture is heated in a reflux apparatus, aldehydic vapours are evolved and dichloroacetal and a small quantity of a product of low boiling point are formed.

Zinc dust acts readily on  $\alpha\beta$ -trichloroethyl ether with formation of dichloroaldehyde and large quantities of hydrogen chloride, but no organo-zinc compound of the formula  $\text{CHCl}_2 \cdot \text{CH}(\text{OEt}) \cdot \text{ZnCl}$  could be obtained.

Reduction of the trichloro-ether by powdered zinc or magnesium and a stream of dry hydrogen chloride, or by zinc and acetic acid, gives mainly dichloroaldehyde, together with a fraction boiling at  $80-90^\circ$  under 10 mm. pressure, which is probably  $\beta\beta$ -dichloroethyl ether.

*Dichloromonothioacetal*,  $\text{SEt} \cdot \text{CH}(\text{OEt}) \cdot \text{CHCl}_2$ , prepared by the interaction of  $\alpha\beta$ -trichloroethyl ether (1 mol.) and ethyl mercaptan (1 mol.), boils at  $110-125^\circ$  under 20–30 mm. pressure.

*Phenylethyldichloroacetal*,  $\text{OEt} \cdot \text{CH}(\text{OPh}) \cdot \text{CHCl}_2$ , obtained by the action of sodium phenoxide on  $\alpha\beta$ -trichloroethyl ether, boils at  $165-170^\circ$  under 40 mm. pressure, reacts energetically with nitric acid, combines with bromine giving a white compound, decolorises permanganate, dissolves in alcohol, and readily decomposes even in a closed vessel in the dark.

$\alpha\beta$ -Trichloroethyl ether (1 mol.) combines with pyridine (1 mol.) forming a substance which, with platinum chloride, gives a compound  $(\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt}, \text{C}_5\text{NH}_5)_2 \cdot \text{PtCl}_4$ , crystallising from dilute hydrochloric acid in orange-yellow needles, melting and decomposing at  $208-209^\circ$ , and, with gold chloride, a yellow compound,

$(\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt}, \text{C}_5\text{NH}_5)_2 \cdot \text{AuCl}_3$ ,  
melting at  $92-93^\circ$ .

T. H. P.

**Course of the Decomposition of Mixed Aliphatic Ethers by Hydrogen Iodide.** ARTHUR MICHAEL and FRANCIS D. WILSON (*Ber* 1906, 39, 2569–2577. Compare da Silva, this Journal, 1876, i, 60 Lippert, Abstr., 1893, i, 620).—When methyl propyl ether is treated with hydrogen iodide at  $0^\circ$ , an additive compound,  $\text{C}_4\text{H}_{10}\text{O}, \text{HI}$ , is formed, which is subsequently decomposed. The products are well washed with water, dried with phosphoric oxide, and fractionated whereby mainly methyl iodide is obtained, the very small quantity of propyl iodide formed being identified in the form of silver propionate.

Ethyl propyl ether yields a similar additive compound,  $\text{C}_5\text{H}_{12}\text{O}, \text{H}$ , which is decomposed at  $100^\circ$ ; from the products, after treatment as above, ethyl and propyl iodides were isolated. The additive compound,  $\text{C}_6\text{H}_{14}\text{O}, \text{HI}$ , obtained from propyl isopropyl ether, is decomposed at  $100^\circ$ , and the products treated as before.

The mixed propyl and isopropyl iodides are converted into the aldehyde and ketone respectively, and identified in the form of the hydrazones.

From considerations of the heats of formation of the alkyl iodides, and also of the energy required to separate the different alkyl groups from oxygen, the authors conclude that an ether containing methyl and a primary or secondary alkyl group will yield methyl iodide and alkylcarbinol by treatment with hydrogen iodide, whilst methyl alcohol and a tertiary alkyl iodide will result from an ether containing the methyl and a tertiary alkyl group. Moreover, an ether containing two primary, two secondary, or two such mixed alkyl groups will yield a mixture of haloids and alcohols containing each of the alkyl groups. C. S.

**Electrolytic Preparation of Alkyloxides and Alkyl-carbonates.** BÉLA SZILÁRD (*Zeit. Elektrochem.*, 1906, 12, 393—395).—When a solution of sodium ethoxide (4 per cent.) in pure anhydrous alcohol is electrolysed with platinum electrodes and a current density just sufficient to produce a small evolution of gas at the anode, sodium ethyl carbonate is formed as a solid deposit at the anode. The yield is about one-seventh of the theoretical quantity. Sodium methyl carbonate is formed in a similar way. Using a magnesium anode, magnesium ethyl (or methyl) carbonate is obtained. Using a lead anode, a one per cent. sodium methoxide solution, and a small current density, lead methoxide,  $\text{Pb}(\text{OMe})_2$  is formed; with higher current densities, salts containing increasing quantities of carbon dioxide are produced. Copper methoxide,  $\text{Cu}(\text{OMe})_2$ , was obtained in a similar way. T. E.

**Preparation of the Anhydrides of Monobasic Organic Acids.** VEREIN FÜR CHEMISCHE INDUSTRIE IN FRANKFURT (D.R.-P. 167304).—When a mixture of chlorine and sulphur dioxide containing a slight excess of the latter gas is passed into a cooled intimate mixture of anhydrous sodium and calcium acetates, acetic anhydride is produced and obtained by distilling the mixture, preferably under reduced pressure (compare Abstr., 1906, i, 3). G. T. M.

**Reactions of Double Decomposition between Alcohols and Esters.** GIUSEPPE BRUNI and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 637—644).—The authors have heated mixtures, in molecular proportions, of menthol with ethyl acetate, ethyl benzoate, ethyl oxalate, or ethyl malonate, in order to determine whether any double decomposition takes place under these conditions, the changes being followed by means of the rotatory power. With ethyl acetate, no change occurs after heating for ten hours at  $100^\circ$ , and the same is the case with ethyl benzoate after twelve hours' heating at  $80^\circ$ . With ethyl oxalate and ethyl malonate, however, double decomposition proceeds at an appreciable velocity when they are heated at  $100^\circ$  with menthol.

With ethyl acetoacetate (2 mols.) and menthol (1 mol.), or with

menthyl acetoacetate (1 mol.), ethyl alcohol (1 mol.), and ethyl acetoacetate (1 mol.), double decomposition takes place, equilibrium being reached after heating at  $100^{\circ}$  for twenty-four hours, when 57.6 per cent. of the menthol has been transformed into menthol acetoacetate. At  $79.9^{\circ}$ , however, equilibrium is not attained, even after 155 hours, although the final condition of equilibrium is the same at this temperature as at  $100^{\circ}$ . The values of  $K$ , calculated according to the equation for a bimolecular reaction, are not constant, but decrease as the time increases.

T. H. P.

**Preparation of Solid Fatty Acids.** CARL DREYMAN (D.R.-P. 166610).—The ordinary process for obtaining solid fatty acids from the unsaturated fatty acids or their glycerides depends on the treatment of these substances with strong sulphuric acid at  $60$ — $120^{\circ}$ , the subsequent washing out of this acid with water or brine solution, and the distillation of the product. The final operation is attended by a certain amount of destructive action due to the decomposition of the hydroxystearic acid which is present. This effect is due to the presence of sulphuric acid, which is tenaciously retained by the organic matter in spite of the washing with water. The distillation may however, be greatly improved by the introduction of some oxide carbonate, or other acid-fixing substance, which neutralises the mineral acid, and thus prevents the formation of hydrocarbons and tar.

G. T. M.

**Measurements of Affinity of Monobasic Unsaturated Fatty Acids.** FRITZ FICHTER and HERMANN MUELLER (*Annalen*, 1906, 348 256—259. Compare Fichter and Pfister, *Abstr.*, 1904, i, 965).—The affinity constants of a number of monobasic  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated fatty acids have been measured by means of the inversion of sucrose and of the hydrolysis of methyl acetate; the results, which are given in the following table, confirm Fichter and Pfister's observation that the  $\beta\gamma$ -unsaturated acids have the larger affinity constants:

	Inversion of sucrose. $K \times 10^{-4}$ .	Hydrolysis of methyl acetate. $K \times 10^{-4}$ .
Butyric acid.....	0.0569	0.0206
Crotonic acid .....	0.0723	0.0320
Vinylacetic acid .....	0.0941	0.0540
<i>n</i> -Valeric acid .....	0.0545	0.0164
$\alpha\beta$ -Pentenoic acid .....	0.0691	0.0170
$\beta\gamma$ -Pentenoic acid .....	0.1738	0.0668
$\alpha$ -Methyl- $\alpha\beta$ -pentenoic acid ..	0.0284	0.0235
$\alpha$ -Methyl- $\beta\gamma$ -pentenoic acid...	0.0757	0.0325

$\alpha$ -Ethyl- $\alpha\beta$ -pentenoic acid has the dissociation constant  $K = 0.0020$  and  $\alpha$ -ethyl- $\beta\gamma$ -pentenoic acid,  $K = 0.00339$ .

The heat of combustion of  $\alpha$ -methyl- $\alpha\beta$ -pentenoic acid is 795.7 Cal. whilst that of  $\alpha$ -methyl- $\beta\gamma$ -pentenoic acid is 797.9 Cal. (compare Thiele, *Abstr.*, 1899, i, 554).

G. Y.

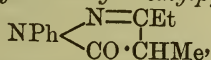


**Transformations of Salts of Pyruvic Acid. IV.** ANNE W. K. DE JONG (*Rec. trav. chim.*, 1906, 25, 229—232. Compare Abstr., 1902, i, 72; 1903, i, 146; 1904, i, 550).—Barium parapyrivate,  $C_6H_6O_6Ba, 4H_2O$ , prepared by the condensation of barium pyruvate spontaneously or by means of baryta, loses  $3H_2O$  when exposed over sulphuric acid. The impurity present in small quantity in barium parapyrivate which has been prepared by the action of potassium cyanide on barium pyruvate is sparingly soluble in boiling water, and dissolves in hydrochloric acid; the solution on evaporation over sulphuric acid and quicklime deposits crystals of a compound which has the empirical formula  $C_7H_8O_7, \frac{1}{2}H_2O$ , and is probably the  $\alpha\gamma$ -lactone of  $\alpha\gamma$ -dihydroxybutane- $\alpha\alpha\gamma$ -tricarboxylic acid,

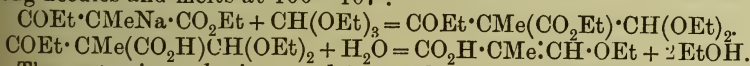


The hydrated compound softens at  $100^\circ$  and decomposes at  $180^\circ$ , the anhydrous compound decomposes at  $195^\circ$ . M. A. W.

**Derivatives of Ethyl Propionylpropionate.** OSKAR EMMERLING and L. KRISTELLER (*Ber.*, 1906, 39, 2450—2455).—When ethyl propionylpropionate is heated with phenylhydrazine on the water-bath and finally at  $140^\circ$ , 1-phenyl-4-methyl-3-ethylpyrazolone,



is obtained; it melts at  $112.5^\circ$  and yields the corresponding salt with hot dilute hydrochloric or sulphuric acid. When heated with methyl iodide and methyl alcohol at  $110^\circ$ , it forms 1-phenyl-2:4-dimethyl-3-ethylpyrazolone,  $C_{13}H_{16}ON_2$ , which melts at  $37.5^\circ$ , boils at  $208—210^\circ$  under 18 mm. pressure, and forms a *platinichloride*,  $2C_{13}H_{16}ON_2, H_2PtCl_6, 2H_2O$ . The interaction of chloroform and the reaction product of sodium and ethyl propionate leads to the formation of  $\beta$ -ethoxymethylacrylic acid,  $OEt \cdot CH : CMe \cdot CO_2H$ , which separates from light petroleum in leaflets or long needles and melts at  $106—107^\circ$ .



The *potassium, barium, calcium, silver, and cadmium* salts are mentioned; the *ethyl* ester boils at  $198—199^\circ$  and has an aromatic odour.

The acid is stable towards cold dilute mineral acids, but by warming yields carbon dioxide, alcohol, and propaldehyde; it absorbs bromine to form a yellow, crystalline additive compound,  $C_6H_{10}O_8Br_2$ .

The constitution of the acid has been verified by its production from  $\beta$ -bromomethylacrylic acid, sodium ethoxide, and alcohol at  $130—140^\circ$ .

Hantzsch and Wohlbrück's acid,  $C_6H_8O_3$  (Abstr., 1887, i, 717), obtained by warming ethyl bromopropionylpropionate, melts, not at  $106—108^\circ$ , but at  $124^\circ$ , and does not yield  $\beta$ -methoxymethylacrylic acid when reduced. C. S.

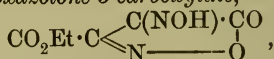
**Crystallographic Description of Alkali Cobaltioxalates.** H. COPAUX (*Chem. Centr.*, 1906, i, 1604; from *Bull. Soc. franç. Min.*, 29, 67—76. Compare Abstr., 1902, i, 586).— $(NH_4)_6Co_2(C_2O_4)_6, 6H_2O$

is monoclinic and isomorphous with the ammonium oxalates of aluminium, chromium, and iron [ $a:b:c=1.0017:1.0:3929$ ;  $\beta=92^{\circ}44'$ ].  $K_6Co_2(C_2O_4)_6, 7H_2O$ , triclinic [ $a:b:c=0.5963:1.0:6590$ ;  $\alpha=88^{\circ}22'$ ,  $\beta=91^{\circ}42'$ ,  $\gamma=101^{\circ}23'$ ].  $Rb_6Co_2(C_2O_4)_6, 8H_2O$ , rhombic [ $a:b:c=1.1485:1.2:5960$ ].  $Na_6Co_2(C_2O_4)_6, 10H_2O$  is monoclinic and isomorphous with the corresponding oxalates of aluminium, chromium, and iron [ $a:b:c=1.398:1.1:293$ ].  $Li_6Co_2(C_2O_4)_6, 12H_2O$  is triclinic and is isomorphous with the lithium oxalates of aluminium and chromium [ $a:b:c=1.0177:1.0:7885$ ;  $\alpha=94^{\circ}22'$ ,  $\beta=81^{\circ}$ ,  $\gamma=109^{\circ}4'$ ].  $K_5Na_{19}Co_8(C_2O_4)_{24}, 32H_2O$  crystallises in pseudoregular octahedra and is isomorphous with the corresponding aluminium and chromium oxalates.  $Rb_3Na_3Co_2(C_2O_4)_6, 5H_2O$  is monoclinic and isomorphous with the corresponding aluminium oxalate [ $a:b:c=1.2211:1.0:8758$ ;  $\beta=91^{\circ}38'$ ]. The crystals of  $(NH_4)_3Na_3Co_2(C_2O_4)_6, 7H_2O$  are monoclinic, but so strongly striated that they cannot be measured.

E. W. W.

**Ethyl Dioximidosuccinate.** ANDRÉ WAHL (*Compt. rend.*, 1906, 143, 56—58).—Ethyl dioximidosuccinate, prepared by the action of hydroxylamine hydrochloride on ethyl dioxysuccinate (Anschütz and Parlato, *Abstr.*, 1892, 1181), is dimorphous, crystallising from a mixture of ether and light petroleum in small, transparent prisms, and in large, transparent crystals which become opaque and white when removed from the mother liquor; the two modifications melt and decompose at  $196^{\circ}$  and are mutually convertible by the action of solvents. It is soluble in boiling water, alcohol, or ether, and insoluble in cold water, and differs from the compound described by Beckh (*Abstr.*, 1897, i, 213), which is soluble in water and melts at  $162^{\circ}$ . Ethyl glyoxime-peroxide-dicarboxylate,  $C_8H_{10}O_6N_2$ , is obtained together with a little ethyl dinitroacetate when ethyl dioximidosuccinate is oxidised with fuming nitric acid, and when treated with ammonia yields the amide,  $(CONH)_4$ , melting at  $250^{\circ}$  (compare Pröpper, *Abstr.*, 1883, 573; Cramer, *Abstr.*, 1892, 699; and Bouveault and Bongert, *Abstr.*, 1903, i, 145).

*Ethyl 4-isonitrosoisooxazolone-3-carboxylate,*



formed as a by-product in the above preparation of ethyl dioximidosuccinate, crystallises in white leaflets, melts and decomposes at  $160\text{--}165^{\circ}$ , is sparingly soluble in water, and yields a characteristic fugitive violet coloration with alkalis.

M. A. W.

**Electrolytic Decomposition of Dicarboxylic Acids: Adipic Acid.** B. LINO VANZETTI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 574—578. Compare *Abstr.*, 1904, i, 141).—In the electrolysis of potassium adipate, a large quantity of carbon dioxide is evolved at the anode, so that the decomposition of the acid is far more profound than has been formerly supposed. The mean and almost constant composition of the gases is: carbon dioxide, 25; unsaturated hydrocarbons

1.5; oxygen, 12; carbon monoxide, 1.5; and hydrogen, 60 per cent. The unsaturated hydrocarbons consist of butylenes of the formulæ  $\text{CH}_2\text{Me}:\text{CH}:\text{CH}_2$  and  $\text{CHMe}:\text{CHMe}$ . The characteristic ethereal odour is due to the secondary formation of alcohols and ethereal salts.

T. H. P.

**$\beta$ -Methylglutaconic Acids.** FRITZ FICHTER and JULIUS SCHWAB (*Annalen*, 1906, 348, 251—256. Compare Feist, this vol., i, 334).—The action of ethyl  $\beta$ -chlorocrotonate or ethyl  $\beta$ -chloroisocrotonate on ethyl sodiomalonate leads to the formation of ethyl  $\beta$ -methylcarboxylglutaconate, which boils at 163—165° under 12 mm. pressure, and on hydrolysis with barium hydroxide yields a mixture of *cis*- and *trans*- $\beta$ -methylglutaconic acids. The *cis*-acid melts at 152°, has a dissociation constant  $K=0.0129$ , and forms salts which crystallise more readily than do those of the *trans*-acid, which melts at 116°, has the dissociation constant  $K=0.0139$ , and is converted partially into the *cis*-form when boiled with aqueous sodium hydroxide (compare Feist, *loc. cit.*). Barium *trans*- $\beta$ -methylglutaconate crystallises with  $5\text{H}_2\text{O}$  ( $6\text{H}_2\text{O}$ ; Genvresse, *Ann. Chim. Phys.*, 1891, [vi], 24, 88). The *anilide* of the *trans*-acid,  $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}$ , melts at 166° and boils at 186° under 14 mm. pressure; the *p*-toluidide,  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}$ , crystallises in long needles, melts at 164°, and boils at 236—240° under 15 mm. pressure.

$\alpha\beta$ -Dibromo- $\beta$ -methylglutaric acid,  $\text{C}_6\text{H}_8\text{O}_4\text{Br}_2$ , formed by the action of bromine under the influence of sunlight on *trans*- $\beta$ -methylglutaconic acid dissolved in a mixture of glacial acetic acid and chloroform, crystallises from a mixture of chloroform and light petroleum and melts at 145°.

G. Y.

**Condensation of Ethyl  $\beta\beta$ -Dimethylglycidate with Ethyl Sodiomalonate. Synthesis of Terebic and Pyroterebic Acids.** ALBIN HALLER and GUSTAVE BLANC (*Compt. rend.*, 1906, 142, 1471—1473).— $\gamma\gamma$ -Dimethyl- $\alpha\beta$ -dicarbethoxybutyrolactone (4-methyl-2:3-dicarbethoxypentan-4-olid),  $\text{CO}_2\text{Et}\cdot\overset{\text{CO}}{\underset{\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}_2}{\text{CH}}}\text{—CO}$ , obtained by the condensation of ethyl  $\beta\beta$ -dimethylglycidate (Darzens, *Abstr.*, 1905, i, 116) with ethyl sodiomalonate, boils at 174° under 12 mm. pressure, crystallises from a mixture of ether and light petroleum in large prisms, melts at 46°, and is converted quantitatively into terebic acid by boiling with hydrochloric acid. The terebic acid was characterised by its conversion into pyroterebic acid and isohexolactone by the action of heat; the phenylhydrazide of pyroterebic acid melts at 106°.

Attempts to effect the condensation of ethyl  $\alpha\beta\beta$ -trimethylglycidate with ethyl sodiomalonate were unsuccessful, owing probably to steric hindrance.

M. A. W.

**Organic Thio-acids. II.** EINAR BIILMANN (*Annalen*, 1906, 348, 120—132. Compare *Abstr.*, 1905, i, 625; Holmberg, *Abstr.*, 1905, i, 323; Klason and Carlson, this vol., i, 232).—Thioglycollic acid is prepared by dissolving xanthoacetic acid in cooled 25 per cent. aqueous ammonia; after twenty-four hours, the mixture is extracted with ether



and heated at  $112^{\circ}$ , made alkaline with ammonia, and again extracted with ether and left overnight in contact with zinc filings; it boils at  $103\text{--}105^{\circ}$  under 14 mm. pressure, and has a sp. gr. 1.326 at  $17.3^{\circ}$ .

Thiolactic acid is prepared from  $\alpha$ -xanthopropionic acid; it boils at  $98.5\text{--}99^{\circ}$  under 14 mm. pressure, and, when cooled with ice-water, crystallises, melting at about  $10^{\circ}$ .

Thiohydracrylic acid, prepared from  $\beta$ -xanthopropionic acid, forms white crystals, melts at  $16.8^{\circ}$ , boils at  $110.5\text{--}111.5^{\circ}$  under 15 mm. pressure, decomposes when heated under the ordinary pressure, and has a sp. gr. 1.218 at  $20.8^{\circ}$ .

$\alpha$ -Xanthoisobutyric acid,  $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , prepared from potassium xanthate and sodium isobutyrate, forms white crystals and melts at  $102\text{--}103^{\circ}$ . When heated with ammonia, it yields  $\alpha$ -thiolisobutyric acid, which is crystalline, melts at  $47^{\circ}$ , boils at  $101\text{--}102^{\circ}$  under 15 mm. pressure, gives an intense indigo-blue coloration with ferric chloride, changing to reddish-violet on addition of ammonia, forms with copper sulphate a yellow, with mercuric chloride or silver nitrate a white precipitate, and is oxidised by iodine, forming  $\alpha$ -dithiodisobutyric acid,  $\text{C}_8\text{H}_{14}\text{O}_4\text{S}_2$ , separating from hot water in colourless crystals.

Disulphidedisuccinic acid,  $\text{S}_2[\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}]_2$ , prepared by the oxidation of thiomalic acid with ferric sulphate and aqueous ammonia, is obtained as a white, crystalline residue. G. Y.

**Organic Thio-acids. III. EINAR BIILMANN** (*Annalen*, 1906, 348, 133—143. Compare preceding abstract; Abstr., 1905, i, 625).—A reply to Holmberg (Abstr., 1905, i, 324).

Trithiocarbodiglycollic acid is formed by the action of sodium chloroacetate on potassium xanthate in hot aqueous solution or by heating alkali xanthoacetates with water. It is decomposed to only a small extent when boiled with water. The sodium salt crystallises with  $2\frac{1}{2}\text{H}_2\text{O}$ .

Carbethoxythioglycollic acid,  $\text{OEt}\cdot\text{CO}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared by the action of potassium thiocarbonate on potassium xanthate, forms colourless, transparent crystals, melts at  $28\text{--}29^{\circ}$ , boils at  $110\text{--}115^{\circ}$  under 20 mm. pressure, is extremely hygroscopic, and is decomposed by alcoholic potassium hydroxide, yielding alcohol, carbon dioxide, and thioglycollic acid, or by alcoholic ammonia, yielding thioglycollic acid and xanthamide. The potassium salt,  $\text{C}_5\text{H}_7\text{O}_4\text{SK}$ , was analysed.

The action of ammonia on xanthoacetic acid leads to the formation of xanthamide, that of aniline to the formation of xanthanilide and *s*-diphenylcarbamide.

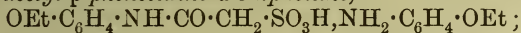
The formation of the reddish-yellow, crystalline potassium trithiocarbonate,  $\text{C}_4\text{H}_2\text{O}_2\text{S}_8\text{K}_6$ , by the successive action of hydrogen sulphide and carbon disulphide on alcoholic potassium hydroxide is confirmed.

G. Y.

**Sulphoacetic Acid. II. Sulphoacetic Acid and Aromatic Amines. OTTO STILLICH** (*J. pr. Chem.*, 1906, [ii], 74, 51—56. Compare this vol., i, 552).—Aniline sulphoacetate,  $(\text{NH}_2\text{Ph})_2\text{C}_2\text{H}_4\text{O}_6\text{S}$ , formed by the action of aniline on aniline hydrogen sulphoacetate, melts at

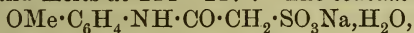
125—151°, decomposes into aniline and sulphoacetic acid when recrystallised from alcohol, and when highly heated yields *aniline acetanilide- $\omega$ -sulphonate*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}\cdot\text{NH}_2\text{Ph}$ , which is formed quantitatively by heating aniline with sulphoacetic acid at 200°; it crystallises from absolute alcohol in long prisms and melts at 229—231°. The *sodium salt*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}\cdot\text{H}_2\text{O}$ , forms nacreous, quadratic leaflets and melts at 283—284°.

*p-Phenetidine sulphoacetate*,  $(\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2\cdot\text{C}_2\text{H}_4\text{O}_5\text{S}$ , crystallises in long, white needles, melts at about 146°, forming a turbid liquid which becomes clear at about 170°, and when highly heated forms *p-phenetidine acetyl-p-phenetidine- $\omega$ -sulphonate*,



this crystallises in needles, commences to sinter at 224°, and melts at 233—240°. The *sodium salt*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$ , crystallises in needles and melts at about 270°, forming a turbid liquid which is not clear at 290°.

*p-Anisidine acetyl-p-anisidine- $\omega$ -sulphonate* forms matted needles, sinters at 220°, and melts at 224—227°. The *sodium salt*,



crystallises in nacreous, rectangular leaflets, commences to soften at about 269°, and gradually decomposes when more highly heated.

The *salt*,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}\cdot\text{NH}_2\cdot\text{C}_7\text{H}_7$ , formed from *o*-toluidine, crystallises in blue, pointed needles, melting at 189—191°; the *sodium salt*,  $\text{C}_9\text{H}_{10}\text{O}_4\text{SNa}\cdot\text{H}_2\text{O}$ , forms prismatic needles and melts at 223—224°.

The *salt*,  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ , formed from  $\alpha$ -naphthylamine, decomposes on recrystallisation; the *sodium salt*,  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$ , forms matted needles and melts at 285—287°.

G. Y.

**Preparation of Aldehydes and Ketones from Alcohols.** W. LANG (D.R.-P. 166357).—The manganic salts are found to be very useful in oxidising alcohols to aldehydes and ketones, inasmuch as the reaction is not carried further when the oxidising agent is in excess.

*Manganous ammonium sulphate*,  $2\text{MnSO}_4\cdot(\text{NH}_4)_2\text{SO}_4$ , obtained in anhydrous crystals by adding excess of ammonium sulphate to a hot acid solution of manganous sulphate, is decomposed by cold water into the double sulphate,  $\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4$ , and manganous sulphate, but when electrolysed in an anode cell lined with lead, the current density being 3.5 amperes per sq. cm., it gives rise to manganic ammonium alum, which is hydrolysed by water, yielding manganic hydroxide.

The mixture thus obtained is employed in oxidising methyl alcohol to formaldehyde, 2.4 parts of the latter being obtained from 4 parts of the alcohol. In a similar manner, 17 parts of menthol yield 14 parts of menthone.

G. T. M.

**Decomposition of Formaldehyde by the Silent Discharge.** FRANZ RUSS (*Zeit. Elektrochem.*, 1906, 12, 412—413).—The silent discharge was passed through the vapour of formaldehyde at 150° and the formation of carbon monoxide and hydrogen observed.

T. E.

**Preparation of a Solid Modification of Chloral.** SIMON GÄRTNER (D.R.-P. 170534).—Chloral hydrate is left for several hours in contact with about half its weight of concentrated sulphuric acid until a white, pasty mass is formed. The acid is then poured off and the residue introduced into well-cooled dilute hydrochloric or sulphuric acid; the product, which now becomes solid, is washed and dried over concentrated sulphuric acid. This product can also be obtained from chloral alcoholate; it is only sparingly soluble in water and becomes quite insoluble when acid is added. It can be employed as an anæsthetic or a hypnotic, and, unlike chloral hydrate, it is devoid of any irritating action on the mucous membrane of the stomach.

G. T. M.

*see errata, V. 96<sup>12</sup>, p. 1266*

**Preparation of Aldehydes, Alcohols, and Acids.** CHEMISCHE FABRIK FLÖRSHEIM, H. MOERDLINGER (D.R.-P. 167137).—The volatile product obtained by blowing air, oxygen, or an ozonised mixture of these gases through heated oils or fats consists of a mixture of the lower aldehydes, alcohols, and aliphatic acids (from  $C_6$  onwards).

Castor oil was heated to  $160^\circ$  and a current of air introduced; a vigorous reaction ensued, raising the temperature to  $220^\circ$ ; the distillate was collected and the oily portion mixed with petroleum and sodium hydrogen sulphite solution and saturated with sulphur dioxide until two clear layers separated. The petroleum extract when shaken with dilute aqueous sodium hydroxide yielded sodium *n*-hexoate and *n*-heptoate, and *n*-heptyl and *n*-octyl alcohols. The sodium hydrogen sulphite solution furnished heptaldehyde.

Similar results were obtained with linseed and rape-seed oils.

G. T. M.

**Formation of Glycerose.** NAZARENO TARUGI (*Gazzetta*, 1906, 36, i, 332—347. See this vol., ii, 631).

[**Alkylenediamine Chromium Compounds.**] PAUL PFEIFFER (*Annalen*, 1906, 346, 26—81. See this vol., ii, 614).

**Antimonichlorides of Dichloro-salts.** PAUL PFEIFFER and M. TAPUACH (*Zeit. anorg. Chem.*, 1906, 49, 437—440. Compare Abstr., 1904, ii, 41).—With the object of elucidating the constitution of the green double chloride of antimony and chromium,  $CrCl_3 \cdot SbCl_5 \cdot 10H_2O$ , described by Weinland and Feige (Abstr., 1903, ii, 218), the authors have prepared and examined two complex antimonichlorides of analogous constitution. The compound,  $[Cr \cdot C_4H_8N_2H_2 \cdot Cl_2][SbCl_5]$ , prepared by the action of antimony pentachloride on violet *cis*-dichlorodiethylenediamine chromium chloride,  $[Cr \cdot C_4H_8N_2H_2 \cdot Cl_2]Cl$ , dissolved in hydrochloric acid, forms violet crystals. The compound,  $[Co \cdot C_4H_8N_2H_2 \cdot Cl_2][SbCl_5]$ , obtained in a similar manner from *trans*-dichlorodiethylenediamine cobalt chloride,  $[Co \cdot C_4H_8N_2H_2 \cdot Cl_2]Cl$ , and antimony pentachloride, forms a green precipitate. The antimony was removed from these double salts by treatment with hydrogen sulphide, and from the respective filtrates derivatives of chromium and cobalt containing two atoms of chlorine were obtained, which proves the constitu-



tion to be as above. From analogy, the formula  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2][\text{SbCl}_5]$  is ascribed to the double chloride of antimony and chromium in agreement with Weinland and Schmid (Abstr., 1905, ii, 326). G. S.

**Compounds of Metallic Thiocyanates with Organic Bases**  
 HERMANN GROSSMANN and BERNHARD SCHÜCK (*Zeit. anorg. Chem.*, 1906, 50, 1—20. Compare this vol., i, 7, 485).—In the present paper, compounds of ethylenediamine with thiocyanates and other salts of bivalent metals are described, and one or two compounds containing  $\alpha$ - and  $\beta$ -naphthylamine have also been prepared. In the majority of cases the compounds were obtained by the direct action of the calculated quantity of base on the salt in aqueous solution; in some cases double decomposition between potassium thiocyanate and the ethylenediamine compound of other salts has been employed. In the course of the investigation it was found that, contrary to Ostwald's opinion (Abstr., 1886, 586), free ethylenediamine, and in some cases the combined base, can be accurately estimated by titration with sulphuric acid, using methyl-orange or litmus as indicator.

*Nickel Compounds.*—*Triethylenediaminenickel thiocyanate*,  
 $(\text{Ni}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2$ ,  
 separates from aqueous solution in violet, prismatic crystals, which melt at  $253^\circ$ . It is decomposed by acids with formation of the corresponding salt of ethylenediamine, and by hot potassium hydroxide, green nickel hydroxide being precipitated. *Diethylenediaminenickel thiocyanate*,  $(\text{Ni}, 2\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2$ , has already been obtained by Werner (Abstr., 1899, i, 857) in two isomeric forms, which crystallise with  $1\text{H}_2\text{O}$  in bluish-violet plates and in reddish-violet needles respectively. The authors confirm Werner's results except that their compounds are anhydrous; both melt at  $220^\circ$ . The nature of the isomerism has not been elucidated. *Ethylenediaminenickel thiocyanate*,

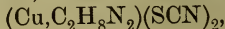
$(\text{Ni}, \text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2$ ,  
 forms bluish-green, rhombic crystals, which melt at  $275^\circ$ . It is also decomposed by hot potassium hydroxide, but is not affected by ammonia. *Triethylenediaminenickel cyanide*,  $(\text{Ni}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{CN})_2$ , prepared by the action of the molecular quantity of solid potassium cyanide on the corresponding thiocyanate, forms reddish-violet crystals, which melt at  $244^\circ$ . *Diethylenediaminenickel chloride*,

$(\text{Ni}, 2\text{C}_2\text{H}_8\text{N}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$ ,  
 occurs in light blue, prismatic crystals, which melt at  $157^\circ$ . The triethylenediamine compound has already been prepared by Werner and Spruck (*loc. cit.*); attempts to obtain the mono-compound were unsuccessful.

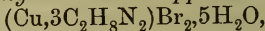
*Zinc and Cadmium Compounds.*—*Triethylenediamine zinc thiocyanate*,  $(\text{Zn}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2$ , forms colourless, rhombohedric crystals, which melt at  $161^\circ$ . The corresponding *cadmium* compound,  $(\text{Cd}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2$ , forms colourless plates which melt at  $138^\circ$ . No other compounds of these metals were obtainable.

*Copper Compounds.*—The three thiocyanates were obtained by double decomposition. *Triethylenediamine copper thiocyanate*,  
 $(\text{Cu}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2 \cdot 5\text{H}_2\text{O}$ ,  
 crystallises in large, deep blue plates, which melt at  $138^\circ$ . The

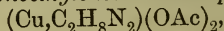
*diethylenediamine* compound,  $(\text{Cu}, 2\text{C}_2\text{H}_8\text{N}_2)(\text{SCN})_2, 2\text{H}_2\text{O}$ , forms dark blue needles, melting at  $83^\circ$ , and the *mono*-compound,



slender, light blue needles. The three compounds just mentioned are not affected by potassium hydroxide or by ammonia. *Ethylenediamine-copper chloride*,  $(\text{Cu}, \text{C}_2\text{H}_8\text{N}_2)\text{Cl}_2, \text{H}_2\text{O}$ , crystallises in reddish-blue leaflets which melt at  $158^\circ$ . With excess of hydrogen chloride, it yields the double *chloride*,  $(\text{Cu}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Cl}_4$ , in golden-yellow leaflets melting at  $272^\circ$ . *Triethylenediaminecopper bromide*,



forms dark blue, lustrous leaflets, the *diethylenediamine* compound,  $(\text{Cu}, 2\text{C}_2\text{H}_8\text{N}_2)\text{Br}_2, 2\text{H}_2\text{O}$ , dark blue, prismatic crystals, and the *monoethylenediamine* compound,  $(\text{Cu}, \text{C}_2\text{H}_8\text{N}_2)\text{Br}_2, \text{H}_2\text{O}$ , lustrous, green plates. *Triethylenediaminecopper acetate*,  $(\text{Cu}, 3\text{C}_2\text{H}_8\text{N}_2)(\text{OAc})_2, 2\text{H}_2\text{O}$ , crystallises in dark blue leaflets, melting at  $67^\circ$ ; *diethylenediamine-copper acetate*,  $(\text{Cu}, 2\text{C}_2\text{H}_8\text{N}_2)(\text{OAc})_2, \text{H}_2\text{O}$ , in light blue, rhombic prisms, melting at  $115^\circ$ ; and *monoethylenediaminecopper acetate*,

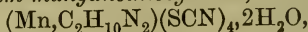


in dark green, lustrous, prismatic crystals. *Monoethylenediaminecopper sulphate*,  $(\text{Cu}, \text{C}_2\text{H}_8\text{N}_2)\text{SO}_4, 3\text{H}_2\text{O}$ , forms slender, light blue needles, which decompose on heating to  $260^\circ$ . *Diethylenediaminecopper nitrate*,  $(\text{Cu}, 2\text{C}_2\text{H}_8\text{N}_2)(\text{NO}_3)_2, 2\text{H}_2\text{O}$ , forms lustrous, dark blue leaflets and melts at  $213^\circ$ .

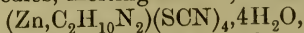
Attempts were made to prepare additive compounds with  $\alpha$ - and  $\beta$ -naphthylamine, but only nickel compounds were obtained.  *$\alpha$ -Naphthylaminenickel thiocyanate*,  $(\text{Ni}, \text{C}_{10}\text{H}_9\text{N})(\text{SCN})_2$ , separates from an alcoholic solution of its components as a moss-green, crystalline precipitate, which decomposes on heating above  $200^\circ$ . The  $\beta$ -compound forms a yellowish-green, crystalline precipitate, which melts about  $261^\circ$ .  
G. S.

**Ethylenediammonium Double Salts.** HERMANN GROSSMANN and BERNHARD SCHÜCK (*Zeit. anorg. Chem.*, 1906, 50, 21—32. Compare Kurnakoff, *Abstr.*, 1898, ii, 475).—These double salts are of the general type  $(\text{M}, \text{C}_2\text{H}_{10}\text{N}_2)\text{X}_4$ , where M is a bivalent metal and X a univalent acid group, and have been prepared either by interaction of the salt of ethylenediamine with the corresponding salt of the metal in aqueous solution, or by dissolving the ethylenediamine additive compound (see preceding abstract) in excess of the corresponding acid.

*Ethylenediammonium manganothiocyanate*,



occurs in long, colourless plates which melt at  $186^\circ$ . The corresponding *ferrous* compound,  $(\text{Fe}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4, 4\text{H}_2\text{O}$ , forms long, brown needles which become oxidised in the air; the *nickel* compound,  $(\text{Ni}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4, 4\text{H}_2\text{O}$ , occurs in green, prismatic crystals and melts at  $95^\circ$ ; the *cobalt* compound,  $(\text{Co}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4, 2\text{H}_2\text{O}$ , in slender, dark blue needles, melting at  $82^\circ$ ; the *zinc* compound,



in slender, colourless needles melting at  $123^\circ$ ; and the *cadmium* compound,  $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4$ , in large, colourless, octahedral crystals which melt at  $182^\circ$ .

*Ethylenediammonium mercurithiocyanate*,  $(\text{Hg}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_4$ , forms colourless, prismatic crystals, which melt at  $120^\circ$ . The compound,  $(\text{Hg}_2, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SCN})_6$ , also forms colourless crystals which melt about  $114^\circ$ .

*Ethylenediammonium cobaltchloride*,  $(\text{Co}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Cl}_4 \cdot 6\text{H}_2\text{O}$ , separates from aqueous solution in lustrous, light green needles which melt at  $254^\circ$ . The corresponding *bromide*,  $(\text{Co}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Br}_4 \cdot 2\text{H}_2\text{O}$ , occurs in slender, light blue needles. *Ethylenediammonium cupribromide*,  $(\text{Cu}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Br}_4 \cdot 5\text{H}_2\text{O}$ , occurs in black, lustrous leaflets which melt at  $242^\circ$ .

*Ethylenediammonium cadmium chloride*,  $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Cl}_4$ , crystallises in colourless, four-sided plates, which melt and decompose at  $300^\circ$ ; the corresponding *bromide*,  $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)\text{Br}_4$ , occurs in colourless, columnar crystals which decompose about  $190^\circ$ .

*Ethylenediammonium uranyl chloride*,  $(\text{UO}_2, \text{C}_2\text{H}_{10}\text{N}_2)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ , forms yellow, prismatic crystals, which are very hygroscopic and melt about  $219^\circ$ .

*Ethylenediammonium ferrous sulphate*,  $(\text{Fe}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , occurs in light green, tabular crystals; *ethylenediammonium cobalt-sulphate*,  $(\text{Co}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , in rose-coloured, triclinic crystals; and *ethylenediammonium manganosulphate*,  $(\text{Mn}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , in faintly rose-coloured crystals. *Ethylenediammonium nickelosulphate*,  $(\text{Ni}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , forms green, triclinic crystals; the corresponding *cadmium* compound,  $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , occurs in colourless, triclinic crystals; the *copper* compound,

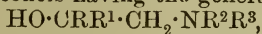
$(\text{Cu}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , in monoclinic crystals; the *zinc* compound,  $(\text{Zn}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , in colourless, monoclinic crystals; and the *magnesium* compound,  $(\text{Mg}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , in small, colourless needles. *Ethylenediammonium aluminosulphate*,  $(\text{Al}_2, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_4 \cdot 4\text{H}_2\text{O}$ , occurs in colourless leaflets. *Ethylenediammonium uranylosulphate*,

$(\text{UO}_2, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , forms small, light yellow, six-sided crystals, which decompose above  $285^\circ$ ; *ethylenediammonium uranylonitrate*,  $(\text{UO}_2, \text{C}_2\text{H}_{10}\text{N}_2)(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ , forms greenish-yellow, four-sided, columnar crystals, which melt about  $215^\circ$  and are strongly fluorescent. The double uranyl nitrate acts on the photographic plate, whilst the double sulphate and chloride have no action on it; on the other hand, the electroscope is affected about equally by the nitrate and the sulphate. The crystals of the double sulphates described in this paragraph have been measured and the results are tabulated.

Attempts were made to obtain double sulphates containing ethylamine, but only the zinc compound was obtained. *Ethylammonium zinc sulphate*,  $(\text{Zn}, 2\text{C}_2\text{H}_5\text{N})(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ , obtained by interaction of ethylamine sulphate and zinc sulphate in aqueous solution, occurs in large, colourless crystals.

G. S.

**Preparation of Aminoalcohols.** J. D. RIEDEL (D.R.-P. 169746, 169819).—The aminoalcohols having the general formula



where R,  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are alkyl or aryl groups, are substances which



may be employed in the production of anæsthetics. The halogen hydrins required for the preparation of these aminoalcohols are readily obtained from chloroacetone and its analogues by the Grignard reaction. The following carbinols were thus obtained for the first time :

*Methylchloromethylpropylcarbinol*,  $\text{CH}_2\text{Cl}\cdot\text{CMePr}^a\cdot\text{OH}$ , boiling at  $75^\circ$  under 35 mm. pressure; *methylchloromethylisobutylcarbinol*,  $\text{CH}_2\text{Cl}\cdot\text{CMe}(\text{C}_4\text{H}_9)\cdot\text{OH}$ , boiling at  $85^\circ$  under 25 mm. pressure; *methylchloromethylisoamylcarbinol*,  $\text{CH}_2\text{Cl}\cdot\text{CMe}(\text{C}_5\text{H}_{11})\cdot\text{OH}$ , boiling at  $96\text{--}98^\circ$  under 23 mm. pressure; *benzylmethylchloromethylcarbinol*,  $\text{CH}_2\text{Cl}\cdot\text{CMe}(\text{C}_7\text{H}_7)\cdot\text{OH}$ , boiling at  $155^\circ$  under 25 mm. pressure; *chloromethyldiethylcarbinol*,  $\text{CH}_2\text{Cl}\cdot\text{CEt}_2\cdot\text{OH}$ , boiling at  $88^\circ$  under 35 mm. pressure.

*Dimethylaminomethyldiethylcarbinol*,  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CEt}_2\cdot\text{OH}$ , obtained by the action of dimethylamine on the last of these chlorohydrins at  $130^\circ$ , is a colourless liquid boiling at  $76\text{--}79^\circ$  under 23 mm. pressure; the *hydrochloride* of its *benzoyl* derivative crystallises from alcohol in well-defined, lustrous plates melting at  $189^\circ$ .

*Dimethylaminodimethylethylcarbinol*,  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{OH}$ , is a colourless liquid boiling at  $57^\circ$  under 23 mm. pressure; the *hydrochloride* of its *benzoyl* derivative melts at  $175^\circ$ .

*Dimethylaminodimethylpropylcarbinol*,  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CMePr}^a\cdot\text{OH}$ , boils at  $78^\circ$  under 35 mm. pressure; its salts are not crystallisable, but the *hydrochloride* of its *benzoyl* derivative separates in very soluble hygroscopic needles melting at  $146^\circ$ .

*Dimethylaminodimethylisobutylcarbinol* boils at  $82^\circ$  under 34 mm. pressure, the *hydrochloride* of the *benzoyl* derivative melts at  $134^\circ$ .

*Dimethylaminodimethylisoamylcarbinol* boils at  $98\text{--}99^\circ$  under 24 mm. pressure; the *hydrochloride* of the *benzoyl* derivative forms silky needles and melts at  $138^\circ$ .

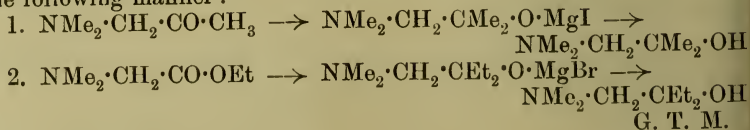
*Phenylmethylaminodimethylcarbinol*,  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{OH}$ , boils at  $135\text{--}138^\circ$  under 31 mm. pressure; its *hydrochloride* melts at  $153^\circ$  and its *dibenzoyl* derivative at  $122^\circ$ .

*Phenyldimethylaminodimethylcarbinol*,  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{OH}$ , boils at  $135\text{--}136^\circ$  under 32 mm. pressure; its *hydrochloride* melts at  $159\text{--}160^\circ$ .

*Phenyldiethylaminodimethylcarbinol*,  $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{OH}$ , is a viscous liquid boiling at  $147\text{--}149^\circ$  under 24 mm. pressure.

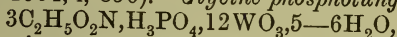
*Benzylmethylaminodimethylcarbinol*,  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{C}_7\text{H}_7)\cdot\text{OH}$  boils at  $144^\circ$  under 24 mm. pressure, the *hydrochloride* of its *benzoyl* derivative melts at  $195^\circ$ .

This series of aminoalcohols can also be prepared by applying the Grignard reaction to the dialkyl-aminoacetones and -aminoesters in the following manner :

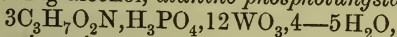


G. T. M.

Phosphotungstates of some Amino-acids. M. BARBER (*Monatsh.*, 1906, 27, 379—401. Compare Gulewitsch, *Abstr.*, 1899, i, 833; Schulze and Winterstein, *Abstr.*, 1902, i, 137; Grossmann and Kraemer, *Abstr.*, 1904, i, 850).—*Glycine phosphotungstate*,



which crystallises in stout prisms and nodular aggregates, and is decomposed by boiling alcohol, *alanine phosphotungstate*,



which crystallises in microscopic, stout, pointed needles, *asparagine phosphotungstate*,  $5C_4H_8O_3N_2, 2H_3PO_4, 22WO_3, 10H_2O$ , and *aspartic acid phosphotungstate*,  $4C_4H_7O_4N, 2H_3PO_4, 20-22WO_3, 24H_2O$ , which crystallises in microscopic octahedra, are prepared by adding 50 per cent. phosphotungstic acid to the hot saturated aqueous solution of the amino-acid, or by dissolving the latter in the phosphotungstic acid solution, so that the proportion present is 1 amino-acid:10 phosphotungstic acid. These four phosphotungstates lose their water of crystallisation at 105°. The phosphotungstate of glycine is soluble to the extent of 4.5, 14.4, and 21.3, of alanine to the extent of 15.7, 19.4, and 27.6, of asparagine, 6.8, 66, and 400, and of aspartic acid, 3, 24, and 400, in water, absolute alcohol, and 80 per cent. alcohol, respectively.

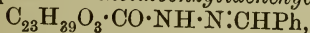
Glutamic acid and phosphotungstic acid yield products which have the approximate composition  $C_5H_9O_4N, 3(H_3PO_4, 12WO_3)$ , or, after recrystallisation from water,  $3C_5H_9O_4N, 2(H_3PO_4, 12WO_3)$ . These are isomorphous mixtures of the phosphotungstate and phosphotungstic acid, and on further recrystallisation from water yield other isomorphous mixtures of varying intermediate composition.

Crystalline phosphotungstates could not be obtained from tyrosine or leucine (compare Kossel and Kutscher, *Abstr.*, 1901, i, 107).

Various methods of separating phosphorus from tungstic acid in organic phosphotungstates are compared. Satisfactory results were obtained only with Sprenger's method (*Abstr.*, 1881, 140) when modified by precipitation of the phosphoric acid by means of ammonium molybdate, instead of ferric chloride and ammonium acetate.

G. Y.

Synthesis of Glycocholic and Taurocholic Acids. S. BONDI and ERNST MÜLLER (*Zeit. physiol. Chem.*, 1906, 47, 499—506).—Pure cholic acid melts at 198° and is most readily prepared by a modification of Mylius' method (*Abstr.*, 1888, 508). The ethyl ester melts at 162°. The *hydrazide*,  $C_{23}H_{39}O_3 \cdot CO \cdot NH \cdot NH_2$ , obtained by heating an alcoholic solution of the ester with hydrazine hydrate, crystallises from hot water in colourless, glistening needles containing water of crystallisation. The anhydrous compound melts at 188—189°, dissolves in most organic solvents, and reduces a cold ammoniacal silver nitrate solution. The solution of the hydrazide in dilute hydrochloric acid yields with benzaldehyde a precipitate of *cholalbenzylidenehydrazine*,



The *azide* of cholic acid,  $C_{23}H_{39}O_3 \cdot CON_3$ , obtained by the action of nitrous acid on the hydrazide, is precipitated as a fine powder,

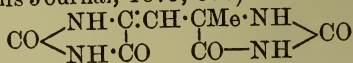
decomposes vigorously at  $73^{\circ}$ , is insoluble in water, but dissolves readily in alcohol or chloroform. The azide condenses with alkaline solutions of glycine and taurine, yielding respectively glyco- and taurocholic acids. J. J. S.

**Preparation of Bromodialkylacetamides.** KALLE & Co. (D.R.-P. 170629).—Ethyl bromodiethylacetate when dissolved in alcohol and shaken for some time with aqueous ammonia yields bromodiethylacetamide, which can be recrystallised from light petroleum. This amide is also obtained by carefully heating ammonium bromodiethylacetate at  $110^{\circ}$  under diminished pressure; ammonium bromodipropylacetate can be converted similarly into bromodipropylacetamide. G. T. M.

**Acyl Derivatives of Cyanamide and Carbamide.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 167138).—Cyanacetic acid or the halogenated acetic acids interact readily with cyanamide or its monoalkyl derivatives. Chloroacetylmethylcarbamide results from the interaction of chloroacetic acid and methylcyanamide in ethereal solution.

*Cyanoacetylmethylcarbamide*,  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$ , obtained in a similar manner from cyanoacetic acid and methylcyanamide crystallises in colourless needles and melts at  $206^{\circ}$ . G. T. M.

**Action of Bromine on  $\alpha$ -Lactylcarbamide and Related Compounds** SIEGMUND GABRIEL (*Annalen*, 1906, 348, 50—90; Compare Abstr., 1905, i, 265; Fischer and Roeder, Abstr., 1902, i, 124; Andreasch, Abstr., 1903, i, 157).—The constitution of pyruvic ureide (Grimaux, this Journal, 1875, 358) is discussed, and



adopted as the most probable.

$\alpha$ -Methylhydantoin ( $\alpha$ -lactylcarbamide) yields pyruvic ureide when heated with 1 mol. of bromine in aqueous solution in a sealed tube on the water-bath. When heated with 1 mol. of bromine in glacial acetic acid solution under varying conditions, it yields pyruvic ureide,  $\alpha$ -bromomethylenehydantoin, and the *hydrobromide* of pyruvic ureide hydrate,  $\text{C}_8\text{H}_{10}\text{O}_5\text{N}_4\cdot\text{HBr}$ ; this crystallises in flat, stout, short prisms, sinters at about  $205^{\circ}$ , and melts and decomposes at  $210$ — $211^{\circ}$ . When treated with water, it is converted into *pyruvic ureide hydrate*,  $\text{C}_8\text{H}_{10}\text{O}_5\text{N}_4\cdot 2\text{H}_2\text{O}$ , which forms glistening, flat needles, loses  $2\text{H}_2\text{O}$  at  $100^{\circ}$ , sinters and becomes yellow at  $233^{\circ}$ , melts and decomposes at  $243$ — $244^{\circ}$ , and yields pyruvic ureide when heated with concentrated sulphuric acid and diluted with water.

$\alpha$ -Bromomethylenehydantoin,  $\text{CO} < \begin{array}{c} \text{NH}\cdot\text{C}\cdot\text{CHBr} \\ \text{NH}\cdot\text{CO} \end{array} >$ , is formed also by

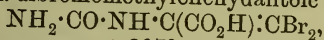
the action of 2 mols. of bromine on  $\alpha$ -methylhydantoin in glacial acetic acid solution on the water-bath; it crystallises in slightly yellow needles, melts and decomposes at  $241$ — $242^{\circ}$ , and is reduced to  $\alpha$ -methylhydantoin by fuming hydriodic acid.

The action of 3 mols. of bromine on  $\alpha$ -methylhydantoin in glacial



acetic acid solution leads to the formation of  $\alpha$ -dibromomethylenehydantoin (Fischer, Abstr., 1887, 918), which is formed also by dissolving tribromopyruvylcarbamide (Fischer, *loc. cit.*) in concentrated sulphuric acid, and is reduced to  $\alpha$ -methylhydantoin by hydriodic acid.

The action of bromine water on  $\alpha$ -bromomethylenehydantoin leads to the formation of  $\alpha$ -dibromomethylenehydantoic acid,



which melts and decomposes at  $207^\circ$  and is identical with Grimaux's dibromodihydromalonylcarbamide (*loc. cit.*), but, contrary to that author's statement, gives a brownish-yellow coloration with dilute ammonia. When heated with concentrated sulphuric acid at  $80^\circ$ , it is converted into  $\alpha$ -dibromomethylenehydantoin. The *methyl* ester,  $\text{C}_5\text{H}_6\text{O}_3\text{N}_2\text{Br}_2$ , formed by heating the above acid with methyl alcohol and hydrogen chloride, crystallises in flat needles and melts at  $208^\circ$ .

When heated with  $\alpha$ -bromomethylenehydantoin and hydrogen bromide in glacial acetic acid solution,  $\alpha$ -methylhydantoin forms pyruvic ureide; the condensation does not take place in the absence of hydrogen bromide.

*Dihydropyruvic ureide*,  $\text{C}_8\text{H}_{10}\text{O}_4\text{N}_4$ , formed with development of heat when pyruvic ureide, or its hydrate, or the hydrobromide of the hydrate is reduced with fuming hydriodic acid, crystallises from boiling water in transparent, flat, pointed, white plates, becomes brown at about  $282^\circ$ , and melts and decomposes at  $299^\circ$ . When hydrolysed with barium hydroxide and water under pressure at  $165^\circ$ , it yields alanine, carbon dioxide, and ammonia; with hydrochloric acid at  $165^\circ$ , it yields ammonia and *dialanine*,  $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CMe}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , which crystallises in thin, hexagonal leaflets or needles, melts and decomposes at  $248$ – $249^\circ$ , forms a readily soluble crystalline *hydrochloride* and a *platinichloride*, is converted into dihydropyruvic ureide by the action of potassium cyanate in aqueous solution, and yields 4N when treated with an excess of barium nitrite and dilute sulphuric acid (Fischer and Koelker, Abstr., 1905, i, 692).

$\alpha\beta$ -Dimethylhydantoin,  $\begin{array}{c} \text{CHMe} \cdot \text{NMe} \\ \text{CO} \text{---} \text{NH} \end{array} > \text{CO}$ , is prepared by shaking ethyl  $\alpha$ -bromopropionate with aqueous methylamine, heating the resulting solution at  $100^\circ$ , evaporating with barium hydroxide, and, after removal of the barium as carbonate, treating the residue with potassium cyanate in aqueous solution. It crystallises in stout, colourless needles, melts at  $120$ – $121^\circ$ , is readily soluble in water, alcohol, ethyl acetate, chloroform, or acetone, less so in ether, and is only sparingly soluble in light petroleum. When treated with 1 mol. of bromine in glacial acetic acid solution, it yields the *hydrobromide* of pyruvic dimethylureide hydrate,  $\text{C}_8\text{H}_8\text{O}_5\text{N}_4\text{Me}_2 \cdot \text{HBr}$ , which crystallises in needles, darkens at  $200^\circ$ , and melts and decomposes at  $285^\circ$ . *Pyruvic dimethylureide hydrate*,  $\text{C}_8\text{H}_8\text{O}_5\text{N}_4\text{Me}_2$ , crystallises in colourless, quadrilateral plates or scales, melts and decomposes at  $255$ – $256^\circ$ , and is reduced by fuming hydriodic acid to *dihydropyruvic dimethylureide*,  $\text{C}_8\text{H}_8\text{O}_4\text{N}_4\text{Me}_2$ , which crystallises in colourless leaflets and melts at  $275$ – $277^\circ$ .

The action of 2 mols. of bromine on  $\alpha\beta$ -dimethylhydantoin in glacial acetic acid solution leads to the formation of  $\beta$ -methyl- $\alpha$ -bromo-

*methylenehydantoin*,  $\text{CO} \begin{array}{c} \text{NMe} \cdot \text{C} \cdot \text{CHBr} \\ | \\ \text{NH} - \text{CO} \end{array}$ , which crystallises in pointed yellow needles, melts at  $143-144^\circ$ , and is readily reduced by hydriodic acid.

$\alpha$ -Bromomethylenehydantoin and  $\alpha\beta$ -dimethylhydantoin interact in presence of hydrogen bromide in glacial acetic acid solution, forming *pyruvic methylureide*,  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CMe} \cdot \text{NMe} \\ | \quad \quad | \\ \text{NH} \cdot \text{CO} \quad \text{CO} - \text{NH} \end{array} \text{CO}$ , which crystallises in microscopic needles or prisms and melts and decomposes at about  $299-300^\circ$ .

$\alpha$ -Ethyl-lacturamic acid,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NEt} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , prepared from ethylamine, ethyl  $\alpha$ -bromopropionate, and potassium cyanate, forms rhombic crystals, melts and decomposes at  $155^\circ$ , and when evaporated with hydrochloric acid yields  $\alpha$ -methyl- $\beta$ -ethylhydantoin (Duvillie Abstr., 1896, i, 89), which crystallises in rhombic plates and melts at  $85^\circ$ . This condenses with  $\alpha$ -bromomethylenehydantoin in presence of hydrogen bromide in glacial acetic acid solution, forming *pyruvic ethylureide*,  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CMe} \cdot \text{NEt} \\ | \quad \quad | \\ \text{NH} \cdot \text{CO} \quad \text{CO} - \text{NH} \end{array} \text{CO}$ , which crystallises in short, pointed prisms and melts and decomposes at  $249^\circ$ .

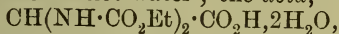
$\alpha$ -Ethylhydantoic acid,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHEt} \cdot \text{CO}_2\text{H}$ , prepared from ethyl  $\alpha$ -bromobutyrate, ammonia, and potassium cyanate, crystallises in quadratic plates and melts and decomposes at  $177^\circ$ .  $\alpha$ -Ethylhydantoin,  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CHEt} \\ | \\ \text{NH} \cdot \text{CO} \end{array}$ , crystallises in leaflets, melts at  $117-118^\circ$ , and on bromination in glacial acetic acid solution yields  $\alpha$ -bromoethylidenehydantoin,  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CBrMe} \\ | \\ \text{NH} \cdot \text{CO} \end{array}$ , which forms rhombic leaflets and melts and decomposes at  $230-236^\circ$ .

Hydantoin is oxidised by bromine in glacial acetic acid solution, forming parabanic acid. The condensation of hydantoin with  $\alpha$ -bromomethylenehydantoin in presence of hydrogen bromide in acetic acid solution leads to the formation of only a small amount of pyruvic ureide.

Malylureide (Guareschi, Abstr., 1878, 138), formed by the action of potassium cyanate on aspartic acid, melts and decomposes at  $224-225^\circ$ , and when treated with bromine in acetic acid solution yields the *acid*,  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{NH} \cdot \text{CO} \end{array}$ , which crystallises in rhombic leaflets, decomposes at  $280-350^\circ$ , forms crystalline *barium* and *silver* salts, is reduced to malylureide by fuming hydriodic acid, and on treatment with bromine water forms  $\alpha$ -dibromomethylenehydantoic acid. G. Y.

**Action of Urethane and of Carbamide on Ethyl Glyoxylate.** **New Synthesis of Allantoin.** LOUIS J. SIMON and J. CHAVANNE (Compt. rend., 1906, 143, 51-54. Compare this vol., i, 396).—*Ethyl diurethaneglyoxylate*,  $\text{CH}(\text{NH} \cdot \text{CO}_2\text{Et})_2 \cdot \text{CO}_2\text{Et}$ , obtained by the condensation of ethyl glyoxylate with urethane, crystallises in colourless transparent prisms, melts at  $143^\circ$ , can be distilled under reduced pressure, dissolves in alcohol, acetic acid, or chloroform, and is stable

in boiling water. The *amide*,  $\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})_2\cdot\text{CO}\cdot\text{NH}_2$ , melts at  $190^\circ$  and is soluble in alcohol or hot water; the *acid*,



obtained from the ester by the action of aqueous or alcoholic potassium hydroxide, crystallises from boiling water in thin, silky needles, melts at  $159\text{--}160^\circ$ , and loses its water of crystallisation at  $110\text{--}115^\circ$ ; the anhydrous acid melts at  $165^\circ$ . Diurethaneglyoxylic acid is much more stable than its higher homologue, diurethanepyruvic acid (this vol., i, 404); it is soluble in alcohol, forms crystalline salts with phenylhydrazine or the aromatic bases, reddens litmus, can be titrated in the presence of phenolphthalein, and is precipitated by mineral acids from a solution of its alkali salt.

Ethyl glyoxylate condenses with carbamide in the presence of hydrogen chloride to form *ethyl allantoate*,  $\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2\cdot\text{CO}_2\text{Et}$ , a white, microcrystalline substance which decomposes at  $200^\circ$ . It is converted into allantoin by the action of ammonia or alkali hydroxides, and in this respect resembles its higher homologue, ethyl homoallantoate (Abstr., 1902, i, 15; 1904, i, 300), from which, however, it differs in its stability towards boiling water, which decomposes ethyl homoallantoate, whilst ethyl allantoate can be recrystallised from that solvent or from boiling alcohol; it is decomposed by acids, regenerating ethyl glyoxylate.

M. A. W.

**Preparation of Aminoguanidine from Nitroguanidine.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 167637).—The electrolytic reduction of nitroguanidine with zinc and platinum electrodes gives unsatisfactory results, but when either a tin cathode is used or a tin salt or finely-divided tin is added to the solution, the yield of aminoguanidine is greatly increased. The nitro-compound is suspended in water slightly acidified with sulphuric acid. A tin cathode with roughened surface is employed and the current density is 250 amperes per sq. metre; the temperature is maintained at  $10^\circ$ , and during the electrolysis just sufficient acid is added from time to time to fix the amine which is being produced; the yield is 81 per cent. of the theoretical.

G. T. M.

**Substances extracted from Muscle. III. Methylguanidine.** WLADIMIR GULEWITSCH (*Zeit. physiol. Chem.*, 1906, 47, 471—475. Compare Abstr., 1900, i, 516; 1905, i, 726; also Kutscher, *Zeit. Nahr. Genussm.*, 1905, 10, 531).—Methylguanidine has been isolated from the extract of muscle. The nitrate of the base melts at  $150^\circ$ . The *picrate*, whether obtained from creatine or from muscle extract, crystallises from water in two distinct modifications: a yellow form crystallising in four- or six-sided pleochroic plates, and an orange-coloured form crystallising in short, four-cornered plates also showing pleochroism. When crystallised under certain conditions, each form can be partially transformed into the other. Guanidine picrate also crystallises in two distinct forms (von Cordier, this vol., i, 486).

J. J. S.

**Action of Sulphides on Nitroprussides.** JUAN F. VIRGILI (*Zeit. anal. Chem.*, 1906, 45, 409—439. Compare Abstr., 1902, ii, 472).—An attempt is made to explain the different colours produced on mixing solutions of sodium nitroprusside with soluble sulphides.



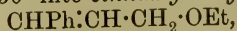
The reddish-yellow, red, purple, and violet shades which are obtained under different conditions are due to the simultaneous formation of two substances, one of which is blue and represents a molecular compound of the sulphide and the nitroprusside, whilst the other (a quaternary nitroprusside) is yellow and is formed by the action of alkali hydroxide on the normal nitroprusside. This view is supported by a study of the absorption spectra. In order to obtain the blue coloration, free alkali hydroxide and alkali salts of weak acids must be absent. It is readily produced when the nitroprusside is added to an excess of a concentrated solution of the sulphide in ethyl alcohol or glycerol, or to an aqueous solution containing excess of hydrogen sulphide. On account of the increasing hydrolysis, a larger excess of hydrogen sulphide is required with increasing dilution, and by reason of the weak basic character of ammonia the blue coloration is more readily obtained with ammonium sulphide than with the alkali metal sulphides. With solutions of the alkali hydrogen sulphides, the colour is distinctly more blue than with corresponding solutions of the normal sulphides. These facts are readily explained by the author's hypothesis.

Experiments on the mixing of solutions under different conditions indicate that the nitroprusside does not react with the sulphide ion but with the non-ionised sulphide. The intensity of the coloration increases when salts with a common ion are added to the solution or when solvents of smaller ionising power are used. The sensitiveness of the nitroprusside as a reagent for sulphide is considerably diminished in consequence of hydrolysis, and addition of substances which decrease the hydrolysis (alkali hydroxides) increases the sensitiveness. Low temperature also increases the sensitiveness; whilst at  $20^{\circ}$  sodium sulphide could be detected at a concentration of 0.0033 gram per litre, it was found that at  $0^{\circ}$  the colour change was given at a concentration of 0.0011 gram per litre. On account of the difficulty of obtaining comparable colorations, nitroprusside is not suitable for the estimation of hydrogen sulphide.

H. M. D.

**Attempts to Synthesise Phenylallene.** AUGUST KLAGES and KARL KLENK (*Ber.*, 1906, 39, 2552—2555).—Cinnamyl chloride obtained from cinnamyl alcohol and hydrogen chloride in the cold boils at  $120^{\circ}$  under 18 mm. pressure, has a sp. gr. 1.101 at  $15^{\circ}/4^{\circ}$ , and, contrary to statements in the literature, forms a *dibromide* which melts at  $104-105^{\circ}$ . When heated with pyridine (2 mols.) it yields a *pyridinium chloride*, which is easily soluble in water and alcohol, and forms a yellow platinichloride and aurichloride, and a white mercurichloride.

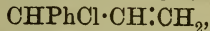
*Cinnamyl bromide*,  $C_9H_9Br$ , obtained from cinnamyl alcohol and hydrogen bromide in glacial acetic acid at  $0^{\circ}$ , melts at  $34^{\circ}$ , boils at  $103^{\circ}$  under 22 mm. pressure, forms with bromine long, white needles of  $\alpha\beta\gamma$ -tribromo- $\alpha$ -phenylpropane, which melts at  $128^{\circ}$ , and is converted by alcoholic potash at  $130^{\circ}$  into *cinnamyl ethyl ether*,



a colourless oil which boils at  $231-232^{\circ}$ .

The reaction between magnesium phenyl bromide and acetaldehyde leads to the formation of  *$\alpha$ -phenylallyl alcohol*,  $OH\cdot CHPh\cdot CH:CH_2$ , a

oil which boils at  $106^{\circ}$  under 18 mm. and at  $214^{\circ}$  under 746 mm. pressure, has a sweet burning taste, and yields with excess of bromine the tribromide previously described. *α-Phenylallyl chloride*,



is a colourless oil with a strong odour; with bromine it forms an additive compound,  $\text{C}_9\text{H}_9\text{ClBr}_2$ , which melts at  $104^{\circ}$ .

*α-Phenylallyl bromide* is a colourless oil with an irritating vapour; it solidifies in ice and is converted by alcoholic potash at  $120^{\circ}$  into *α-phenylallyl ethyl ether*,  $\text{CH}_2 : \text{CH} \cdot \text{CHPh} \cdot \text{OEt}$ , an oil which has a faint fruity odour and boils at  $203\text{--}205^{\circ}$  under 755 mm. pressure. C. S.

**Condensation Products of cyclopentadiene.** JOHANNES THIELE and HANS BALHORN [in part with WALTHER ALBRECHT] (*Annalen*, 1906, 348, 1—15. Compare Thiele, Abstr., 1900, i, 298; this vol., i, 569, 586).—Methylethylfulvene (Engler and Frankenstein, Abstr., 1901, i, 658), prepared by the condensation of cyclopentadiene with methyl ethyl ketone in presence of sodium ethoxide in cooled alcoholic solution, boils at  $62.5^{\circ}$  under 13 mm. pressure, volatilises with ether vapour, gives a red coloration and a light precipitate with glacial acetic-sulphuric acid, and resinifies when exposed to air.

*Diethylfulvene*,  $\begin{matrix} \text{CH} : \text{CH} \\ \text{CH} : \text{CH} \end{matrix} > \text{C} : \text{CEt}_2$ , prepared in the same manner from cyclopentadiene and diethyl ketone, boils at  $74.5\text{--}78.5^{\circ}$  under 19 mm. pressure and closely resembles dimethylfulvene in its colour, odour, and reactions.

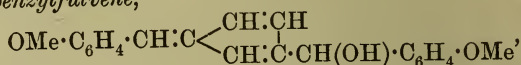
A product,  $\begin{matrix} \text{CH} : \text{CH} \\ \text{CH} : \text{CH} \end{matrix} > \text{C} : \text{C} < \begin{matrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{matrix} > \text{O}$ , is formed together with dimethylfulvene by the condensation of acetone with cyclopentadiene in alcoholic sodium ethoxide or concentrated methyl-alcoholic potassium hydroxide solution, or with dimethylfulvene in presence of alcoholic sodium ethoxide; it is obtained as a dark orange oil which boils at  $110^{\circ}$  under 11 mm. pressure.

Freshly-distilled dimethylfulvene solidifies quickly when cooled with ice, forming yellow crystals melting at about  $4^{\circ}$ , but after four to five months the oil solidifies only slowly and the yellow crystals change at the ordinary temperature into *bisdimethylfulvene*,  $\text{C}_{16}\text{H}_{20}$ , which crystallises from alcohol in hexagonal plates or needles, melts at  $83^{\circ}$ , yields dimethylfulvene when heated above its melting point, is not resinified by air, gives a yellowish-red coloration with concentrated sulphuric acid, reduces potassium permanganate immediately in alcoholic solution, and forms an additive compound with 2 mols. of bromine. *isoNitroso-dimethylfulvene*,  $\text{C}_5\text{H}_4 : \text{CMe} \cdot \text{CH} : \text{NOH}$ , prepared from *isonitrosoacetone* and cyclopentadiene, crystallises in glistening, reddish-brown needles or prisms, melts at  $87^{\circ}$ , has a characteristic odour, reduces ammoniacal silver and Fehling's solutions when heated, and is dissolved and decomposed by warm dilute sulphuric acid.

*Cinnamylidenecyclopentene*,  $\text{C}_5\text{H}_4 : \text{CH} \cdot \text{CH} : \text{CHPh}$ , formed by condensation of cyclopentadiene and cinnamaldehyde in presence of methyl-alcoholic potassium hydroxide, crystallises in bluish-red needles, melts at  $102^{\circ}$ , is rapidly oxidised by moist oxygen, gives a violet to blue

coloration with concentrated sulphuric acid, forms an *additive* compound with bromine, and is reduced by aluminium amalgam to an oil which readily resinifies.

The condensation of *cyclopentadiene* with anisaldehyde leads to the formation of *p-methoxyphenylfulvene* and *p-methoxyphenyl- $\alpha$ -hydroxy-p-methoxybenzylfulvene*,

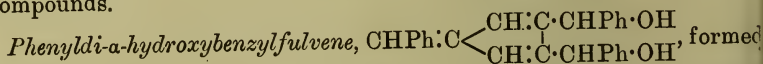


which crystallises in sheaves of red prisms, melts at  $129^\circ$ , is readily oxidised, and with concentrated sulphuric acid gives a deep blue coloration becoming red.

*p-Methoxyphenylfulvene*,  $\text{C}_5\text{H}_4 : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , crystallises in short, red spears, melts at  $70^\circ$ , and gives an orange coloration with concentrated sulphuric acid.

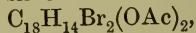
*p-Methoxybenzylcyclopentene*,  $\text{C}_5\text{H}_5 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , formed by reduction of the last substance with aluminium amalgam in moist ether, is obtained as a light orange oil, which on cooling deposits a small amount of white crystals melting at  $163^\circ$ . The oil boils at  $153$ — $154^\circ$  under 9 mm. pressure, and solidifies to glistening, colourless crystals melting at  $53^\circ$ . It forms an *additive* compound with bromine, and gives an orange coloration with concentrated sulphuric acid.

The yellow, insoluble condensation product of *cyclopentadiene* with formaldehyde contains a polymeride of fulvene together with oxygen compounds.



by the condensation of *cyclopentadiene* with benzaldehyde, crystallises in red needles, melts at  $178$ — $179^\circ$ , absorbs bromine, and gives a violet coloration with concentrated sulphuric acid.

*Diphenylfulvene dibromide*,  $\text{C}_{18}\text{H}_{14}\text{Br}_2$ , crystallises in yellow plates, melts at  $102$ — $102.5^\circ$ , and decomposes on exposure to air. The *tetrabromide*,  $\text{C}_{18}\text{H}_{14}\text{Br}_4$ , forms yellow plates, melts at  $123^\circ$ , dissolves in boiling aniline, alcohol, or glacial acetic acid, forming red solutions, gives a green coloration when reduced with zinc dust in chloroform or benzene, is decomposed by alcoholic alkali hydroxides, and forms silver bromide when heated with silver nitrate solution. The *diacetate*,



formed by boiling the tetrabromide with potassium acetate in glacial acetic acid solution, crystallises in white leaflets and melts at  $166$ — $167^\circ$ . *See also* V. 942 p. 12, p. 1477

G. Y.

So-called *Aromatic Substances containing Six Atoms of Carbon*. ~~G. Y.~~ KÖRNER (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 525—526).—In the chemistry of the halogen- and nitro-substitution products of benzene there are still many gaps, besides which many incorrect data have been published. The author proposes to fill up the gaps in, and revise generally, the knowledge of the formation and properties of aromatic compounds containing six carbon atoms, with a view to ascertaining the influence of the nature and position of each substituent atom or group of atoms on the ultimate properties of the molecule (compare following abstract).

T. H. P.



*See entry V. 942 p. 2*  
*Wilhelm No. 1477*  
**The Sixth Dibromonitrobenzene.** GEORG KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 526—528).—On treating *o*-dibromobenzene with nitric acid of sp. gr. 1·54, adding concentrated nitric acid, and subsequently pouring the product of the reaction into water, a mixture of 3:4-dibromo-1-nitrobenzene and 2:3-dibromo-1-nitrobenzene is obtained. By extracting with 95 per cent. alcohol and cooling the solution, the former is separated and, after a single crystallisation, melts at 57—58°.

Concentration of the alcoholic mother liquors yields a crystalline mixture melting at 42° and, on treating this with acetic acid, 2:3-dibromo-1-nitrobenzene is obtained; it crystallises from acetic acid or ethyl acetate in thick, monoclinic prisms [*E. REPOSSI*:  $a:b:c = 1.031:1.0282$ ;  $\beta = 80^{\circ}8'30''$ ], melts at 85·2° and dissolves readily in acetone or chloroform, and to a less extent in ether; on replacing the nitro-group by an amino-residue and the latter by a bromine atom, 1:2:3-tribromobenzene, melting at 87·4°, is obtained; when treated with alcoholic ammonia solution at 180°, 2:3-dibromo-1-nitrobenzene yields 2-bromo-6-nitroaniline, which crystallises in pale yellow needles melting at 73·4°, dissolves moderately easily in alcohol, volatilises readily in a current of steam, and is converted by the action of ethyl nitrite into *m*-bromonitrobenzene. When acted on by a mixture of concentrated sulphuric acid and nitric acid of sp. gr. 1·54, 2:3-dibromo-1-nitrobenzene gives a mixture of three dinitro-derivatives.

2:3-Dibromoaniline, prepared by the action of a hydrochloric acid solution of stannous chloride (3 mols.) on 2:3-dibromo-1-nitrobenzene, crystallises from aqueous alcohol in colourless, transparent plates melting at 43°, dissolves readily in alcohol, ether, or ethyl acetate, distils easily in a current of steam, and is a less energetic base than the other *o*-dibromoaniline.

2:3-Dibromoacetanilide, prepared by boiling 2:3-dibromoaniline with acetic anhydride, is slightly soluble in alcohol, from which it separates in acicular crystals melting at 164°.

3-Bromo-2-iodo-1-nitrobenzene, prepared from the bromonitroaniline melting at 73·4° by replacing the amino-group by an iodine atom, forms faintly green, transparent, monoclinic prisms [*E. REPOSSI*:  $a:b:c = 0.634:1:0.568$ ;  $\beta = 74.56^{\circ}$ ], melting at 119—120°.

2-Chloro-3-bromo-1-nitrobenzene crystallises from alcohol or ether in green, flattened needles melting at 65°.

T. H. P.

**New Case of Form-analogy and Miscibility of Position-isomeric Benzene Derivatives and the Crystalline Forms of the Six Dibromonitrobenzenes.** FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 26—33).—2:3-Dibromo-1-nitrobenzene crystallises in small, flat, sherry-coloured needles belonging to the triclinic system [ $a:b:c = 1.4778:1:1.9513$ ;  $\alpha = 90^{\circ}45\frac{2}{3}'$ ,  $\beta = 110^{\circ}36\frac{3}{4}'$ ,  $\gamma = 89^{\circ}59\frac{1}{4}'$ ]; the crystals show a decided approach to the monoclinic system. 2:5-Dibromo-1-nitrobenzene forms small, pale yellow, lustrous, flattened, triclinic plates [ $a:b:c = 1.4909:1:2.0214$ ;  $\alpha = 90^{\circ}57\frac{1}{2}'$ ,  $\beta = 113^{\circ}21\frac{1}{3}'$ ,  $\gamma = 90^{\circ}2'$ ]. The two compounds, although closely related, are not isomorphous, but can form an interrupted series of mixed crystals. The binary melting-point curve possesses

a eutectic point at  $52^{\circ}$  with two per cent. of the compound with higher melting point. The mixed crystals contain up to 48 per cent. of the 1:2:3-derivative and melt between  $75^{\circ}$  and  $84.5^{\circ}$ .

The 2:4-dibromo-1-nitrobenzene also crystallises in the triclinic system [ $a:b:c = 1.1307:1:1.1698$ ;  $\alpha = 97^{\circ}36'$ ,  $\beta = 113^{\circ}37'$ ,  $\gamma = 87^{\circ}33'$ ], but does not form mixed crystals.

The 2:6:1-, 3:5:1-, and 3:4:1-derivatives belong to the monoclinic system. They do not form mixed crystals in binary mixtures, the lower melting point being lowered on addition of the component melting at the higher temperature. The differences in the crystalline forms of the brominated derivatives are much less than those between the corresponding chlorinated compounds. E. F. A.

**Preparation of 1:2-Dichloro-4-nitrobenzene.** K. OEHLEB (D.R.-P. 167297).—Polyhalogenated nitro-derivatives of aromatic hydrocarbons are generally obtained by nitrating the halogen compounds; the converse operation, the chlorination of the nitro-compound, has not been successfully performed on a technical scale. One part of anhydrous ferric chloride was added to 20 parts of fused *p*-nitrochlorobenzene and chlorine introduced at  $95$ — $110^{\circ}$ , until the additional weight of the mixture corresponded with 4.5 parts; the mixture was added to water, when a theoretical yield of 1:2-dichloro-4-nitrobenzene was obtained, which, after one crystallisation, gave the correct melting point ( $43^{\circ}$ ). The ferric chloride may be replaced by other chlorine carriers, such as iron, phosphorus, antimony pentachloride, or iodine. G. T. M.

**Crystallographic Characters of some Organic Compounds** FRANS M. JAEGER (*Zeit. Kryst. Min.*, 1906, 42, 158—169).—Crystallographic determinations are given of the following compounds: *o*-nitrobenzyl-*o*-toluidine, diphenylhydrazine, 2:4:6-trinitro-*m*-xylene, 4:5:6-trinitro-*m*-xylene, 2:5:6-trinitro-*m*-xylene, 2:3:5-trinitro-*p*-xylene, 1:2-dichloro-3-nitrobenzene, 1:3-dichloro-2-nitrobenzene, 1:3-dichloro-5-nitrobenzene, and 1:4-dichloro-2-nitrobenzene. L. J. S.

**Reduction of Aromatic *o*- and *p*-Dinitro-compounds.** JAKOB MEISENHEIMER and EGBERT PATZIG (*Ber.*, 1906, 39, 2526—2532 Compare Meisenheimer, *Abstr.*, 1904, i, 150).—The sodium salt  $C_6H_4O_4N_2Na_2$ , formed by reduction of *p*-dinitrobenzene by means of hydroxylamine hydrochloride and sodium methoxide in methyl-alcoholic solution, separates almost quantitatively as a red, crystalline powder, detonates slightly when heated, and dissolves and decomposes in aqueous sodium hydroxide.

The volume of nitrogen evolved on reduction of *o*-dinitrobenzene by hydroxylamine in methyl-alcoholic sodium hydroxide solution agrees with that required by the equation  $C_6H_4(NO_2)_2 + 2NH_2 \cdot OH + 2KOH = C_6H_4(NO_2K)_2 + 4H_2O + N_2$ . The sodium salt,  $C_6H_4O_4N_2Na_2$ , is obtained as a red, amorphous powder if the reduction takes place in benzene methyl-alcoholic solution; it dissolves in water or alcohol, forming a dark blue solution, and when treated with bromine in dilute solution at  $0^{\circ}$  yields *o*-nitronitrosobenzene as a light yellow precipitate. On passage of a current of carbon dioxide, the blue methyl-alcoholic solution of the sodium salt becomes red and sodium hydrogen carbonate

is deposited, the blue solution being again formed on heating. If the solution is diluted with water and saturated with carbon dioxide, *o*-dinitrobenzene is formed slowly.

*o*-Nitronitroso-*p*-xylene,  $C_8H_8O_3N_2$ , is prepared by reducing the mixture of *o*- and *m*-dinitro-*p*-xylene obtained by the direct nitration of *p*-xylene (Jannasch and Stuenkel, Abstr., 1881, 808) with hydroxylamine hydrochloride in methyl-alcoholic potassium hydroxide solution, extracting the unchanged *m*-dinitro-compound with ether, and adding hydrochloric acid to the cooled solution; it forms slightly yellow crystals, melts at  $130.5^\circ$ , dissolves in hot benzene, chloroform, or glacial acetic acid to green, in alcoholic alkali hydroxides to red solutions, and does not form a condensation product with aniline in glacial acetic acid solution.

G. Y.

**Phenylnitrolic Acid.** HEINRICH WIELAND and LEOPOLD SEMPER (*Ber.*, 1906, 39, 2522—2526).—*Phenylnitrolic acid*,  $NO_2 \cdot CPh : NOH$ , is prepared by the successive action of sodium nitrite and oxalic acid on potassium phenylnitromethane in aqueous solution at  $-15^\circ$ ; it crystallises from light petroleum in slender, colourless needles, has a bitter flavour, melts at  $57-58^\circ$ , and decomposes when heated a few degrees above its melting point or more slowly in alkaline solution, forming nitrous acid and benzonitrile oxide (Werner and Buss, Abstr., 1894, i, 585), which rapidly polymerises to diphenylglyoxime peroxide. This crystallises in glistening, colourless leaflets, melts and decomposes at  $114-116^\circ$  ( $105^\circ$ , Beckmann, Abstr., 1889, 980), and gives Liebermann's nitroso-reaction.

When oxidised carefully with potassium permanganate in alkaline solution, phenylnitrolic acid yields benzenylnitrosolic acid (this vol., i, 412).

G. Y.

**Behaviour of Sulphonic Acids on Oxidation by Fusion.** CARL GRAEBE and HERMANN KRAFT (*Ber.*, 1906, 39, 2507—2512. Compare this vol., i, 255).—When fused with lead peroxide and potassium hydroxide, sulphonic acids are oxidised to the following products, the yields being given in percentages of the theoretical.

*p*-Toluenesulphonic acid : benzoic acid (78 per cent.) and *p*-hydroxybenzoic acid (2—3 per cent.). *p*-Toluenesulphonamide, 8 per cent. of which remains unchanged : benzoic acid (26.6 per cent.) and *p*-hydroxybenzoic acid (34.7 per cent.). *o*-Toluenesulphonic acid : benzoic acid and *o*-cresol. *o*-Toluenesulphonamide : benzoic acid, *o*-cresol, salicylic acid, and traces of an acid insoluble in chloroform. *o*-Xylene-4-sulphonic acid : phthalic acid (70.5 per cent.). *m*-Xylene-4-sulphonic acid is oxidised only with difficulty : isophthalic acid (33 per cent.) and traces of benzoic and *m*-toluic acids. *p*-Xylenesulphonic acid : terephthalic acid (11 per cent.), *p*-xylenol (26—28 per cent.), and traces of hydroxyterephthalic or salicylic acid. Mesitylenesulphonic acid : trimesic acid (55 per cent.) containing uvitic acid. *p*-Ethylbenzenesulphonic acid : benzoic acid (10 per cent.) and *p*-hydroxybenzoic acid (15 per cent.). *m*-Sulphobenzoic acid : *m*-hydroxybenzoic acid (97 per cent.).

When boiled with aqueous potassium hydroxide and then fused with an anhydrous alkali hydroxide, *o*-tolylsulphone yields benzoic acid (93 per cent.) and a small quantity of an oil having an odour of cresol.



When fused directly with potassium hydroxide, *o*-tolylsulphone is oxidised to benzoic acid and *o*-cresol, the fused mass smelling of benzaldehyde.

When fused with potassium hydroxide, benzaldehyde-4-sulphonic acid yields benzoic (40 per cent.) and *p*-hydroxybenzoic (54 per cent.) acids, benzaldehyde-2-sulphonic acid yields *o*-cresol and benzoic (36.5 per cent.) and salicylic (52 per cent.) acids, whilst *o*-sulphobenzoic acid yields salicylic acid quantitatively. G. Y.

**Combination of Mercuric Iodide with Free Amines**  
MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1906, [vi], 24, 21—24).—A general consideration of facts already recorded (this vol., i, 484) Mercuric iodide combines not only with methylamine (*loc. cit.*), but also with aromatic bases; with aniline the compound  $2\text{NH}_2\text{Ph}\cdot\text{HgI}_2$  is obtained, and with pyridine the compound  $2\text{C}_5\text{NH}_5\cdot\text{HgI}_2$ . The interaction is best effected by warming an alcoholic solution of the base with mercuric iodide; the salt separates in crystals on cooling. The compounds are also formed as a crystalline precipitate by the action of an aqueous solution of the base on a concentrated solution of potassium iodide saturated with mercuric iodide. W. A. D.

**Action of Bromine on Aromatic Amines. Substitution Products and Perbromides.** KARL FRIES (*Annalen*, 1906, 346, 128—219. Compare Abstr., 1904, i, 571).—On bromination, aromatic amines yield at the ordinary temperature either substitution products or perbromides according to the conditions. The presence of acid is unfavourable to the introduction of bromine into the nucleus. Additive products, perbromides, are produced in the presence of hydrogen halides before substitution takes place, and are converted readily into the substitution products. Perbromides of six types have been observed,  $\text{X}_2\text{Br}$ ,  $\text{XBr}$ ,  $\text{X}_2\text{Br}_3$ ,  $\text{XBr}_2$ ,  $\text{XBr}_4$ , and  $\text{XBr}_6$ , where X represents the hydrobromide of a base. Hydrochlorides form perbromides of the types  $\text{XBr}$  and  $\text{XBr}_2$ . Hydriodides form perbromides most, and hydrochlorides least, readily. The salts of quaternary bases show the greatest tendency to form perbromides, and the primary amines the least; but the number and nature of the substituting groups exercise a very great influence. The perbromides of unsubstituted bases are very unstable; they can only be obtained by adding bromine at a low temperature to the hydrobromide of the base suspended in hydrobromic acid. Partially substituted amines, on the other hand, yield well-crystallised stable perbromides. The perbromides give up bromine to all substances reacting with bromine, and in the presence of solvents are generally converted into substitution products, when this is possible. Most dry perbromides give up bromine to the air, the higher bromides passing over into the lower perbromides, some of which (those derived from quaternary salts) are stable under these conditions. All perbromides are decomposed by water. When substitution is not possible, oxidation takes place. The perbromides of secondary and tertiary amines lose, with water, an alkyl group, primary or secondary amines being produced. 2:4-Disubstituted tertiary amines behave similarly, but here substitution also takes place, thus:  $\text{C}_6\text{H}_3\text{X}_2\cdot\text{NMe}_2, \text{HBr}, \text{Br}_2 = \text{C}_6\text{H}_2\text{X}_2\text{Br}\cdot\text{NHMe}, \text{HBr} + \text{BrMe}$ .

The diperbromide of *p*-bromodimethylaniline hydrobromide behaves in a unique manner; it yields *p*-bromodimethylaniline, 2:4-dibromodimethylaniline, and the perbromide of diphenquinonetetramethyldiiminium dibromide,  $\text{Br}_2\cdot\text{NMe}_2\text{Br}:\text{C}_6\text{H}_4:\text{C}_6\text{H}_4:\text{NMe}_2\text{Br}, \text{Br}_2$ , which can also be obtained directly by the action of bromine on *p*-bromodimethylaniline.

All the perbromides are similarly constituted, a complex negative ion being present.

The perbromides of all quaternary and many tertiary amines cannot be converted into substitution products, a fact which is in agreement with the direct bromination of aromatic amines. With one mol. of bromine, aniline yields a mixture of mono-, di-, and tri-bromoanilines; methylaniline yields a mixture of mono- and di-bromomethylanilines, and dimethylaniline yields quantitatively bromodimethylaniline. With 2 mols. of bromine, aniline gives the same mixture, monomethylaniline exclusively a dibromo-derivative, and dimethylaniline, dibromodimethylaniline, but with difficulty. Three mols. of bromine convert aniline and methylaniline into the tribromo-derivatives, but transform dimethylaniline into tribromomethylaniline, a methyl group being eliminated. Similar changes are observed if bromine acts on an amine in which a hydrogen atom in the ortho- or the para-positions is already replaced. An alkyl group appears to protect one of the ortho-hydrogen atoms, whilst two alkyl groups prevent both the ortho-hydrogen atoms from being replaced.

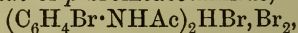
The influence of a bromine atom in the ortho-position relatively to the amino-group on the introduction of alkyl groups has also been investigated. All halogenated amines are less readily alkylated than unsubstituted amines; if the halogen is in the ortho-position with respect to the amino-group, the reaction is still further retarded. Thus, excess of methyl iodide and sodium carbonate alkylated, in thirty hours, 30 per cent. of 2:4-dibromoaniline, 15 per cent. of 3:5-dibromo-*p*-toluidine, and 0 per cent. of *s*-tribromoaniline. Similarly, in the addition of methyl iodide to a tertiary base, it was found that *p*-bromodimethylaniline yielded thirty times as much quaternary iodide as *o*-bromodimethylaniline. Diortho-substituted bases cannot be converted into quaternary bases. It cannot be concluded with certainty that these facts are accounted for by steric hindrance of the reactions.

Large excess of strong acids prevents substitution. Since quaternary salts are also incapable of being substituted, it is argued that the first step in the process of substitution of amines is an addition of the substituting agent to the nitrogen atom.

The *perbromide*,  $\text{NH}_2\text{Ph}, \text{HBr}, \text{Br}_2$ , is prepared by adding a mixture of bromine and concentrated hydrobromic acid to a mixture of aniline, acetic acid, and hydrobromic acid; it forms yellow crystals, which are reconverted into aniline by treatment with sodium hydrogen sulphite; treated with water or other solvents or on exposure to the air, bromoanilines are formed. *s*-Tribromoaniline yields the *perbromide*,  $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NH}_2, \text{HBr}, \text{Br}_2$ , when bromine is added to its solution in acetic acid; it crystallises in garnet-red prisms melting

and decomposing at  $105^{\circ}$ ; the fused mass resolidifies and again melts at  $205^{\circ}$ ; all the bromine is eliminated by treatment with solvents or keeping in the air. 3:5-Dibromo-*o*-toluidine gives under the same conditions the *perbromide*,  $C_6H_2MeBr_2 \cdot NH_2, HBr, Br_2$ , which forms dark red prisms, losing bromine at  $120^{\circ}$  and melting at  $240^{\circ}$ . The corresponding *derivative* of dibromo-*p*-toluidine crystallises in brownish-red plates, which lose bromine at  $110^{\circ}$  and melt at  $225^{\circ}$ . *Diacetyl-5-bromo-1:3:4-xylidine*, prepared by prolonged boiling of 5-bromo-*m*-xylidine with acetic anhydride, crystallises in prisms melting at  $59^{\circ}$ . 6-Bromo-1:3:4-xylidine is the chief product of the bromination of *m*-xylidine in concentrated sulphuric acid; its *diacetyl* derivative crystallises in plates melting at  $70^{\circ}$ . 5:6-Dibromo-1:3:4-xylidine,  $C_6HMe_2Br_2 \cdot NH_2$ , is better prepared from 6-bromo- than from 5-bromo-*m*-xylidine; it crystallises in needles melting at  $40^{\circ}$ . Its *monoacetyl* derivative crystallises in needles melting at  $192^{\circ}$ , and its *diacetyl* derivative in prisms melting at  $183^{\circ}$ . *m*-Xylidine in hydrobromic acid yields the *perbromide*,  $C_6H_3Me_2 \cdot NH_2, HBr, Br_2$  (?), which appears to be identical with the compound mistaken by Fischer and Windaus (Abstr., 1900, i, 484) for a bromoamine; it crystallises in yellow needles, which readily lose bromine, and is converted by contact with solvents into bromoxylidine. The *perbromide*,  $C_6H_2Me_2Br \cdot NH_2, HBr, Br_2$ , obtained from 5-bromoxylidine, crystallises in plates melting at  $134^{\circ}$ .

When acetanilide is treated with 1 mol. of bromine in glacial acetic acid, a *perbromide* of *p*-bromoacetanilide,



is obtained as yellow plates melting at  $135^{\circ}$ ; on addition of water during the bromination the *perbromide* is decomposed, *p*-bromoacetanilide alone being formed. In order to form 2:4-dibromoacetanilide, dilute acetic acid should be used and sodium acetate added. *s*-Tribromoacetanilide can only be obtained in a yield of 15 per cent. when acetanilide is brominated.

When 1:3:4-acetxylidide is brominated, besides the 6-bromo-derivative both the 5- and the 2-bromo-derivatives are produced.

2:4-Dibromomethylaniline,  $C_6H_3Br_2 \cdot NHMe$ , prepared by brominating methylaniline in acetic acid and then cautiously adding water, crystallises in leaflets melting at  $48^{\circ}$ . 2:4:6-Tribromomethylaniline, prepared similarly, crystallises in needles melting at  $39^{\circ}$ , boils at  $310^{\circ}$ , and forms a very sparingly soluble hydrochloride and hydrobromide; the *platinichloride* crystallises in orange plates decomposing at  $232^{\circ}$ , and the *acetyl* derivative in plates melting at  $101^{\circ}$ . The *perbromide* of dibromomethylaniline,  $(C_6H_3Br_2 \cdot NHMe, HBr)_2, Br_2$ , is prepared either from dibromomethylaniline or from bromomethylaniline in the presence of hydrobromic acid, and crystallises in yellowish-red prisms melting at  $125^{\circ}$ ; it is converted into tribromomethylaniline by treatment with water. The *perbromide*,



crystallises in prisms, becoming colourless at  $100^{\circ}$  and melting at  $190^{\circ}$ . The *perbromide* from tribromomethylaniline,  $C_6H_2Br_3 \cdot NHMe, HBr, Br_2$ , crystallises in brownish-red needles melting at about  $160^{\circ}$ ; addition of water to its solution in acetic acid converts it into tribromoaniline. The *perbromide*,  $C_6H_2Br_3 \cdot NHMe, HCl, Br_2$ , forms yellowish-red plates



which melt at  $150^{\circ}$  and change in the air into the hydrochloride of *s*-tribromomethylaniline, which crystallises in prisms decomposing at  $190^{\circ}$ ; water converts this perbromide into *s*-tribromoaniline.

*5-Bromomethyl-o-toluidine*,  $C_6H_3MeBr \cdot NHMe$ , prepared from methyl-*o*-toluidine, is an oil boiling at  $165^{\circ}$  under 25 mm. pressure; the corresponding 3:5-dibromo-compound boils at  $187^{\circ}$  under 50 mm. pressure, and yields a *hydrobromide* which darkens at  $180^{\circ}$  and melts at  $220^{\circ}$ . The *perbromide*,  $C_6H_3MeBr \cdot NHMe, HBr, Br_2$ , prepared directly from methyl-*o*-toluidine, crystallises in red prisms decomposing at  $105^{\circ}$ , and is converted by warming with solvents into dibromo-toluidine. The *perbromide*,  $C_6H_2MeBr_2 \cdot NHMe, HBr, Br_2$ , obtained from 3:5-dibromomethyltoluidine, crystallises in prisms melting at  $142^{\circ}$  and is converted by water into 3:5-dibromo-*o*-toluidine.

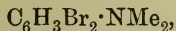
*p-Bromoethylaniline*,  $C_6H_4Br \cdot NHEt$ , prepared from ethylaniline, melts at  $12^{\circ}$ ; 2:4-dibromoethylaniline crystallises in plates melting at  $51^{\circ}$ ; 2:4:6-tribromoethylaniline, prepared directly from ethylaniline, crystallises in needles melting at  $45^{\circ}$ . The *perbromide*,  $C_6H_3Br_2 \cdot NHEt, HBr, Br_2$ , prepared from 2:4-dibromoethylaniline in the presence of hydrobromic acid, crystallises in yellowish-red plates melting at  $85^{\circ}$ , and when warmed with acetic acid passes into tribromoethylaniline. The *perbromide*,  $C_6H_2Br_3 \cdot NHEt, HBr, Br_2$ , crystallises in yellowish-brown prisms melting at  $125^{\circ}$ , and when heated with dilute acetic acid is converted into tribromoaniline.

3-Bromoethyl-*p*-toluidine,  $C_6H_3MeBr \cdot NHEt$ , is an oil boiling at  $143^{\circ}$  under 25 mm. pressure; its *hydrobromide* crystallises in prisms decomposing at about  $160^{\circ}$ . 3:5-Dibromoethyl-*p*-toluidine is an oil boiling at  $169^{\circ}$  under 20 mm. pressure; its *hydrobromide* crystallises in needles melting at  $185^{\circ}$ . The *perbromide*,



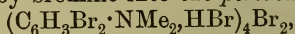
crystallises in golden-yellow needles melting at  $110^{\circ}$ , and is converted into 3:5-dibromo-*p*-toluidine by warming with water.

*p*-Bromodimethylaniline is formed easily from dimethylaniline and bromine in acetic acid solution; its *hydrobromide* crystallises in prisms melting at  $105^{\circ}$  and decomposing at  $185^{\circ}$ , and the *hydriodide* forms crystals melting at  $145^{\circ}$ . 2:4-Dibromodimethylaniline,



is prepared by treating dimethylaniline with excess of bromine in acetic acid solution and then decomposing the perbromide thus formed with sodium acetate, or directly by methylating dibromoaniline or dibromomethylaniline; it is an oil boiling at  $275^{\circ}$  under 740 mm. pressure; its *stannochloride* crystallises in plates decomposing at  $240^{\circ}$ , and its *platinichloride* in golden-yellow needles melting at  $237^{\circ}$ ; the *hydrobromide* crystallises in prisms. 2:4:6-Tribromodimethylaniline, prepared by methylating tribromomethylaniline with methyl sulphate and magnesium oxide, is an oil boiling at  $301^{\circ}$  under 750 mm. pressure; it reacts with bromine, giving tribromomethylaniline, but not with methyl iodide or methyl sulphate; the *platinichloride* crystallises in prisms sintering at  $180^{\circ}$  and melting at  $190^{\circ}$ . The *perbromide* from dimethylaniline,  $NPhMe_2, HBr, Br_2$ , forms reddish-brown crystals which are easily reduced to dimethylaniline and are readily converted into *p*-bromodimethylaniline. The *perbromide*,

$(C_6H_4Br \cdot NMe_2, HBr)_2Br_2$ , is prepared directly from dimethylaniline in acetic acid solution, and forms dark red crystals, sintering at  $95^\circ$  and melting at  $107^\circ$ . The *perbromide*,  $C_6H_4Br \cdot NMe_2, HBr, Br_2$ , is formed when 1 mol. of dimethylaniline and 2 mols. of bromine are used; it crystallises in dark red plates sintering at  $75^\circ$  and melting at  $85^\circ$ ; on keeping in the air it passes over into the *perbromide* last mentioned. With water it yields the dibromodimethylaniline and the *perbromide* of diphenoquinonetetramethyldi-iminium dibromide; the latter is also formed from bromine and tetramethylbenzidine; it is a brownish-red powder melting at about  $158^\circ$ , is reduced to tetramethylbenzidine, and is coloured bluish-green by alkali hydroxides. Tetramethylbenzidine also gives with bromine a dark green, amorphous compound,  $C_{16}H_{20}N_2Br_2$ , which sinters at  $70^\circ$  and melts at  $90^\circ$ , and is reduced to tetramethylbenzidine; concentrated sulphuric or hydrochloric acids give red, crystalline products, and bromine converts it into the *perbromide* last mentioned. Dibromodimethylaniline hydrobromide is converted by bromine into the *perbromide*,



which crystallises in green plates melting at  $135^\circ$ . The same salt also yields the *perbromide*,  $C_6H_3Br_2 \cdot NMe_2, HBr, Br_2$ , which crystallises in prisms melting at  $102^\circ$ . The *perbromide*,  $C_6H_2Br_3 \cdot NMe_2, HBr, Br_2$ , prepared from tribromodimethylaniline, crystallises in pale yellowish-red needles melting at  $124^\circ$ , and is converted by water into tribromomethylaniline.

5-Bromodimethyl-o-toluidine,  $C_6H_3MeBr \cdot NMe_2$ , boils at  $246^\circ$ , its *platinichloride* crystallises in golden-yellow prisms decomposing at  $240^\circ$ . 3:5-Dibromodimethyl-o-toluidine, prepared by alkylating dibromotoluidine, is an oil boiling at  $277^\circ$  under 751 mm. pressure; it does not react either with methyl iodide or methyl sulphate, and when treated with bromine in acetic acid solution yields *dibromomethyltoluidine*, a methyl group being eliminated; the last-mentioned base is also directly produced by the action of bromine on dimethyl-o-toluidine, and decomposing the *perbromide* first formed with sodium acetate; it is an oil boiling at  $185$ – $187^\circ$  under 50 mm. pressure, and forms a *hydrobromide* which crystallises in plates decomposing at  $220^\circ$ . Dimethyl-o-toluidine forms the *perbromide*,  $C_6H_4Me \cdot NMe_2, HBr, Br_2$ , which crystallises in needles or plates melting at  $68^\circ$ , and is converted by treatment with solvents into 5-bromodimethyl-o-toluidine. The *perbromide*,  $(C_6H_3MeBr \cdot NMe_2, HBr)_2Br_2$ , prepared from 1 mol. of dimethyl-o-toluidine and  $1\frac{1}{2}$  mols. of bromine, crystallises in dark red needles and is converted by water into a mixture of bromodimethyl- and dibromomethyl-o-toluidine. The *perbromide*,



obtained from dimethyl-o-toluidine and 2 mols. of bromine, crystallises in plates or prisms melting at  $85^\circ$  and decomposing at  $140^\circ$ . The *perbromide*,  $C_6H_2MeBr_2 \cdot NMe_2, HBr, Br_2$ , crystallises in yellowish-red needles melting at  $112^\circ$ , and is converted by water into dibromomethyltoluidine.

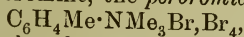
3-Bromodimethyl-p-toluidine, prepared by brominating dimethyl-p-toluidine, is an oil boiling at  $239^\circ$  under 750 mm. pressure, and is converted by bromine into the 3:5-dibromomonomethyl-p-toluidine, which

boils at  $154^{\circ}$  under 16 mm. pressure. 3:5-Dibromodimethyl-*p*-toluidine, prepared by methylating the dibromotoluidine, is an oil boiling at  $270^{\circ}$  under 750 mm. pressure. The *perbromide*,  $C_6H_2MeBr_2 \cdot NMe_2, HBr, Br_2$ , crystallises in prisms melting at  $130^{\circ}$ , and on treatment with water loses methyl bromide.

2:4-Dibromodiethylaniline,  $C_6H_3Br_2 \cdot NEt_2$ , formed on treating with sodium acetate the *perbromide* produced by the action of bromine on diethylaniline, is an oil boiling at  $285^{\circ}$  under 751 mm. pressure; it is converted by further treatment with bromine into *s*-tribromoaniline; its *platinichloride* crystallises in yellowish-red prisms melting at  $207^{\circ}$ , and its *stannochloride* forms crystals melting at  $235^{\circ}$ . The *perbromide*,  $NPhEt_2, HBr, Br_2$ , is a red oil, which is converted by water into *p*-bromodiethylaniline. The *perbromide*,  $(C_6H_4Br \cdot NEt_2, HBr)_2 Br_2$ , crystallises in prisms melting at  $75^{\circ}$ , and is converted by water into 2:4-dibromodiethylaniline and a quinonoid derivative of tetraethylbenzidine. Diethylaniline also yields the *perbromide*,  $(C_6H_4Br \cdot NEt_2, HBr)_4 Br_6$ , which crystallises in red prisms melting at  $81^{\circ}$ .

4:4'-Dibromodiphenylmethylamine,  $C_{13}H_{11}NBr_2$ , prepared from diphenylmethylamine and bromine, crystallises in needles melting at  $120^{\circ}$ . 2:2':4:4'-Tetrabromodiphenylmethylamine,  $C_{13}H_9NBr_4$ , prepared by warming the *perbromide* formed from diphenylmethylamine with the solvent, crystallises in prisms melting at  $142^{\circ}$ ; bromine converts it into tetrabromodiphenylamine. Dibromodiphenylmethylamine yields a *perbromide*,  $(C_6H_4Br)_2 NMe, HBr, Br_2$  (?), which forms red crystals, and is transformed by solvents into a mixture of tetrabromodiphenylmethylamine and tetrabromodiphenylamine.

The *perbromide*,  $NPhMe_3Br, Br_4$ , prepared from phenyltrimethylammonium bromide, crystallises in bluish-red prisms melting at  $40^{\circ}$ , and is converted into the dibromide on exposure to the air. *p*-Tolyltrimethylammonium bromide crystallises in prisms melting at  $219^{\circ}$ , and is converted by bromine into the *perbromide*,  $C_6H_4Me \cdot NMe_3Br, Br_2$ , which forms yellow, four-sided plates melting at  $113^{\circ}$ , from which, by further treatment with bromine, the *perbromide*,



is obtained; it forms dark red crystals melting at  $45^{\circ}$ . K. J. P. O.

**Crystalline Forms of the 2:4-Dinitroaniline Derivatives Substituted in the  $NH_2$ -Group.** FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 23—25).—The melting points, molecular weights, equivalent volumes in the solid state, symmetry, axial elements, and topic parameters of 31 derivatives of 2:4-dinitroaniline are recorded in tabular form. The substances all have the same family character, only a few showing no simple relationship to the rest.

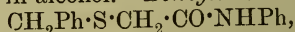
E. F. A.

**Nitration of Acetanilide.** ARNOLD F. HOLLEMAN and C. H. SLUITER (*Rec. trav. chim.*, 1906, 25, 208—212).—The authors have examined the products of the nitration of acetanilide in order to determine if the quantity of the secondary products is affected by the concentration of the nitric acid employed (compare Körner, this Journal, 1876, i, 204);

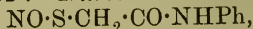


the results show that when acetanilide is slowly added to ten times its weight of nitric acid of sp. gr. 1.46 at 0°, the product is pure *p*-nitroacetanilide; if nitric acid of a higher specific gravity is employed 2:4-dinitroacetanilide is formed as a secondary product, the quantity increasing with the increase in the concentration of the nitric acid but no *o*-nitroacetanilide is produced (compare Körner, *loc. cit.* Beilstein and Kurbatoff, *Annalen*, 1879, 197, 83); if, however, acetanilide is added rapidly to nitric acid of sp. gr. 1.52, a small quantity of *o*-nitroacetanilide is formed owing to the increase in temperature caused by the more violent reaction. M. A. W.

**Thio-fatty Anilides.** HEINRICH BECKURTS and GUSTAV FRERICH (*J. pr. Chem.*, 1906, [ii], 74, 25—50. Compare Abstr., 1902, i, 763 —[With L. HARTWIG.])—*Methylthiolacetanilide*,  $\text{SMe} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$  prepared by the action of methyl iodide and alcoholic potassium hydroxide on thioglycollanilide in a sealed tube in the water-bath crystallises in colourless leaflets, melts at 74°, and is readily soluble in alcohol or ether. *n-Propylthiolacetanilide*,  $\text{SPr}^a \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$  crystallises in colourless needles and melts at 57°. *iso-Propylthiolacetanilide*,  $\text{SPr}^b \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , forms flat needles and melts at 67°. *Ethylenedithioldiacetanilide*,  $\text{C}_2\text{H}_4(\text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh})_2$ , crystallises in colourless needles, melts at 158°, and is only sparingly soluble in alcohol. *Propylenedithioldiacetanilide*,  $\text{C}_3\text{H}_6(\text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh})_2$ , forms colourless needles and melts at 154—155°. *Carboxymethylthiolacetanilide*,  $\text{CO}_2\text{Me} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , formed from methyl chlorocarbonate and thioglycollanilide, crystallises in colourless needles, melts at 83° and is readily soluble in alcohol. *Benzylthiolacetanilide*,

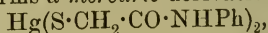


forms colourless, flat needles, melts at 73.5°, and is readily soluble in alcohol. *Benzylidenedithioldiacetanilide*,  $\text{CHPh}(\text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh})_2$ , formed by the action of benzaldehyde or of benzylidene dichloride on potassium hydroxide on thioglycollanilide, crystallises in colourless needles and melts at 182°. *Nitrosothiolacetanilide*,



formed by the action of potassium nitrite and hydrochloric acid on thioglycollanilide in aqueous solution, crystallises in red needles, decomposes when heated, yielding nitric oxide and dithioglycollanilide and is readily soluble in alcohol or ether.

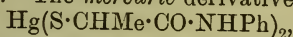
Thioglycollanilide forms a *mercuric* derivative,



which crystallises in glistening leaflets and decomposes when heated and a *mercurichloride*,  $\text{HgCl} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , which is obtained as a yellowish-white, crystalline powder, insoluble in the ordinary solvents.

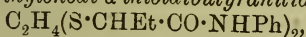
*α-Methylthiolpropanilide*,  $\text{SMe} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NHPh}$ , formed by the action of methyl iodide and potassium hydroxide on *α*-thiolpropanilide in alcoholic solution, crystallises in glistening, colourless needles and melts at 126°. *α-n-Propylthiolpropanilide*,  $\text{SPr}^a \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NHPh}$  crystallises in needles and melts at 92°. *α-iso-Propylthiolpropanilide*,  $\text{C}_{12}\text{H}_{17}\text{ONS}$ , forms colourless needles melting at 84°. *Ethylenedithioldipropanilide*,  $\text{C}_2\text{H}_4(\text{S} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NHPh})_2$ , crystallises in colourless needles melting at 172—174°. *Propylenedi-α-thioldipropanilide*,

$C_2H_6(S \cdot CHMe \cdot CO \cdot NHPh)_2$ , forms a slightly yellow, viscid oil. *α*-Carboxymethylthiolpropanilide,  $CO_2Me \cdot S \cdot CHMe \cdot CO \cdot NHPh$ , crystallises in glistening leaflets and melts at  $103.5^\circ$ . *α*-Benzylthiolpropanilide,  $CH_2Ph \cdot S \cdot CHMe \cdot CO \cdot NHPh$ , crystallises in colourless, flat needles and melts at  $119.5^\circ$ . *Benzylidenedi-α-thioldipropanilide*,  $CHPh(S \cdot CHMe \cdot CO \cdot NHPh)_2$ , forms colourless needles and melts at  $187^\circ$ . *α-Nitrosothiolpropanilide*,  $NO \cdot S \cdot CHMe \cdot CO \cdot NHPh$ , is obtained as an unstable red oil. The mercuric derivative,



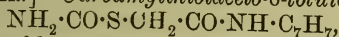
separates from glacial acetic acid in small crystals and melts and decomposes above  $200^\circ$ . The mercurichloride,  $HgCl \cdot S \cdot CHMe \cdot CO \cdot NHPh$ , forms a crystalline powder and melts and decomposes at  $110-120^\circ$ .

*α-Methylthiolbutyranilide*,  $SMe \cdot CHEt \cdot CO \cdot NHPh$ , crystallises in colourless needles and melts at  $111-112^\circ$ . *α-isoPropylthiolbutyranilide*,  $SPr^i \cdot CHEt \cdot CO \cdot NHPh$ , forms colourless, flat needles and melts at  $87-88^\circ$ . *Ethylenedi-α-thioldibutyranilide*,



forms colourless crystals melting at  $125^\circ$ . *Propylenedi-α-thioldibutyranilide*,  $C_3H_6(S \cdot CHEt \cdot CO \cdot NHPh)_2$ , is obtained as a viscid, yellow oil which gradually crystallises. *α*-Carboxymethylthiolbutyranilide,  $CO_2Me \cdot S \cdot CHEt \cdot CO \cdot NHPh$ , forms colourless needles melting at  $82^\circ$ . *α-Benzylthiolbutyranilide*,  $CH_2Ph \cdot S \cdot CHEt \cdot CO \cdot NHPh$ , crystallises in colourless needles melting at  $89^\circ$ . *Benzylidenedi-α-thioldibutyranilide*,  $CHPh(S \cdot CHEt \cdot CO \cdot NHPh)_2$ , forms colourless leaflets melting at  $148^\circ$ . *α-Nitrosothiolbutyranilide*,  $NO \cdot S \cdot CHEt \cdot CO \cdot NHPh$ , is obtained as an unstable red oil. The mercuric derivative,  $Hg(S \cdot CHEt \cdot CO \cdot NHPh)_2$ , and the mercurichloride,  $HgCl \cdot S \cdot CHEt \cdot CO \cdot NHPh$ , form micro-crystalline powders which decompose when heated.

[With CARL BEYER.]—*Carbamylthiolaceto-o-toluidide*,

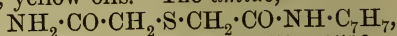


prepared by heating chloroacetic acid and *o*-toluidine with potassium thiocyanate in aqueous solution, crystallises in colourless needles, melts at  $123-124^\circ$ , and when dissolved in hot 10 per cent. ammonia and precipitated by hydrochloric acid in an atmosphere of carbon dioxide yields *thiolaceto-o-toluidide*,  $SH \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$ , which crystallises in colourless needles, melts at  $84-85^\circ$ , and is readily soluble in alcohol. *Dithiodiaceto-o-toluidide*,  $S_2(CH_2 \cdot CO \cdot NH \cdot C_7H_7)_2$ , crystallises in colourless needles melting at  $164-165^\circ$ . The following derivatives of *thiolaceto-o-toluidide*, in which  $R = S \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$ , have been prepared; the temperatures given are melting points: *methyl*-,  $Me \cdot R$ : colourless leaflets,  $65-66^\circ$ ; *ethyl*-,  $Et \cdot R$ : colourless needles,  $60-61^\circ$ ; *ethylenedi*-,  $C_2H_4R_2$ : colourless nodules,  $184-185^\circ$ ; *dimethylmethylenedi*-,  $CMe_2R_2$ : colourless leaflets,  $160-161^\circ$ ; *n-propyl*-,  $Pr \cdot R$ , colourless needles,  $57-58^\circ$ ; *isopropyl*-,  $CHMe_2R$ : colourless needles,  $61-62^\circ$ ; *benzyl*-,  $CH_2Ph \cdot R$ : colourless needles,  $74-75^\circ$ ; *carboxymethyl*-,  $CO_2Me \cdot R$ : colourless needles,  $90-91^\circ$ ; *carboxyethyl*-,  $CO_2Et \cdot R$ : colourless needles,  $78-79^\circ$ .

*Thioldiaceto-o-toluidamic acid*,  $CO_2H \cdot CH_2 \cdot S \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$ , formed from chloroacetic acid and *thiolaceto-o-toluidide*, crystallises in colourless nodules, melts at  $125-126^\circ$ , and is readily soluble in alcohol.

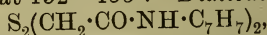
The *methyl*,  $CO_2Me \cdot CH_2 \cdot S \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$ , and *ethyl*,  $CO_2Et \cdot CH_2 \cdot S \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$ ,

esters form viscid, yellow oils. The *amide*,



forms colourless needles and melts at 150—151°. Thioldiacetoditoluidide, formed from thiolaceto-*o*-toluidide and chloroacetyl-toluidide, is identical with Gröthe's product from chloroacetyl-toluidide and potassium hydrogen sulphide (Abstr., 1901, i, 79).

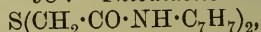
*Thiolaceto-m-toluidide*,  $\text{SH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , crystallises in colourless needles and melts at 152—153°. *Dithiodiaceto-m-toluidide*,



forms colourless needles and melts at 162—163°. The following derivatives of thiolaceto-*m*-toluidide, in which  $\text{R} = \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , are described; the temperatures given are melting points:

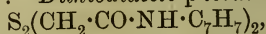
*Carbamyl-*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{R}$ : colourless needles, 151—152°; *methyl-*,  $\text{Me} \cdot \text{R}$ : colourless needles, 52—53°; *ethyl-*,  $\text{Et} \cdot \text{R}$ : a yellow oil; *ethylenedi-*,  $\text{C}_2\text{H}_4\text{R}_2$ : colourless needles, 127—128°; *hydroxyethyl-*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{R}$ : colourless needles, 89—90°; *dimethylmethylenedi-*,  $\text{CMe}_2\text{R}_2$ : colourless leaflets, 141—142°; *benzyl-*,  $\text{CH}_2\text{Ph} \cdot \text{R}$ : colourless needles, 39—40°; *carboxymethyl-*,  $\text{CO}_2\text{Me} \cdot \text{R}$ : a viscid oil; *carboxyethyl-*,  $\text{CO}_2\text{Et} \cdot \text{R}$ : colourless leaflets, 82—83°.

*Thiodiaceto-m-toluidamic acid*,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , forms colourless leaflets melting at 99—100°. The *methyl*,  $\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}$ , and *ethyl*,  $\text{C}_{13}\text{H}_{17}\text{O}_3\text{NS}$ , esters are obtained as viscid, yellow oils. The *amide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , crystallises in colourless nodules and melts at 97—98°. *Thiodiaceto-m-toluidide*,



crystallises in colourless needles and melts at 135—136°.

*Thiolaceto-p-toluidide*,  $\text{C}_9\text{H}_{11}\text{ONS}$ , crystallises in colourless needles and melts at 125—126°. *Dithiodiaceto-p-toluidide*,



crystallises in colourless needles and melts at 180—182°. The following derivatives of thiolaceto-*p*-toluidide,  $\text{R} = \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , are described; the temperatures given are melting points:

*Carbamyl-*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{R}$ : colourless leaflets, 196°; *methyl-*,  $\text{Me} \cdot \text{R}$ : colourless needles, 102—103°; *ethyl-*,  $\text{Et} \cdot \text{R}$ : colourless needles, 84—85°; *ethylenedi-*,  $\text{C}_2\text{H}_4\text{R}_2$ : colourless needles, 194—195°; *hydroxyethyl-*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{R}$ : colourless needles, 87—88°; *dimethylmethylenedi-*,  $\text{CMe}_2\text{R}_2$ : colourless needles, 182—183°; *n-propyl-*,  $\text{Pr}^n \cdot \text{R}$ : colourless needles, 80—81°; *isopropyl-*,  $\text{Pr}^i \cdot \text{R}$ : colourless needles, 66—67°; *benzyl-*,  $\text{CH}_2\text{Ph} \cdot \text{R}$ : colourless needles, 73—74°; *benzylidenedi-*,  $\text{CHPhR}_2$ : colourless needles, 185—186°; *carboxymethyl-*,  $\text{CO}_2\text{Me} \cdot \text{R}$ : 96—97°; *carboxyethyl-*,  $\text{CO}_2\text{Et} \cdot \text{R}$ : colourless needles, 126—127°.

*Thiodiaceto-p-toluidamic acid*,  $\text{C}_{11}\text{H}_{13}\text{O}_3\text{NS}$ , forms colourless crystals and melts at 101—102°. The *methyl* ester,  $\text{C}_{12}\text{H}_{15}\text{O}_3\text{NS}$ , melts at 38—39°; the *ethyl* ester,  $\text{C}_{13}\text{H}_{17}\text{O}_3\text{NS}$ , melts at 46—47°; the *amide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , crystallises in colourless leaflets and melts at 148—149°.

G. Y.

Direct Introduction of Amino-groups into the Nucleus of Aromatic Nitro-compounds. JAKOB MEISENHEIMER and EGBER PATZIG (*Ber.*, 1906, 39, 2533—2542).—The action of hydroxylamine



hydrochloride on *m*-dinitrobenzene in alcoholic sodium ethoxide solution leads to the formation of a light red *sodium* salt,  $C_6H_3O_6N_4Na_2$ , which detonates slightly when heated or on contact with a small quantity of water, is more stable in the presence of an alkali hydroxide, and on acidification yields *m*-dinitrobenzene. The cooled aqueous solution of the sodium salt gradually deposits *m*-dinitro-*m*-phenylenediamine, whilst the diluted aqueous-alcoholic solution yields *m*-dinitro-*m*-phenylenediamine, *m*-dinitrobenzene, and 2:4-dinitroaniline, which is converted into *m*-dinitro-*m*-phenylenediamine by the further action of hydroxylamine.

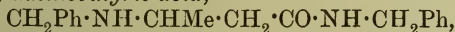
The *sodium* salt,  $C_7H_{11}O_9N_6Na_3 \cdot 3H_2O$ , obtained in the same manner from *s*-trinitrobenzene as an intensely red, granular precipitate, gradually decomposes in a vacuum, forming ammonia, detonates when heated, and yields picramide and *s*-trinitro-*m*-phenylenediamine on addition of an acid to its aqueous solution at 0°.

2:6-Dinitro-3-toluidine,  $C_7H_7O_4N_3$ , is obtained in a 10—15 per cent. yield by the action of hydroxylamine hydrochloride on 2:6-dinitrotoluene in methyl-alcoholic potassium hydroxide solution at 30° and addition of much water to the resulting solution; it forms glistening, yellow crystals, melts at 132.5°, and is readily soluble in alcohol.

2-Nitro- $\alpha$ -naphthylamine is formed in the same manner from 3-nitronaphthalene; if the product is allowed to remain in contact with the reaction solution, it is converted slowly into 2-nitro- $\alpha$ -naphthol.

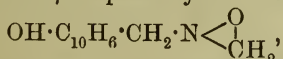
The action of hydroxylamine on ethyl *m*-nitrobenzoate in concentrated, alkaline, absolute alcoholic solution leads to the formation of the *sodium* salt of *m*-nitrobenzhydroxamic acid,  $C_7H_5O_4N_2Na$ ; the acid melts at 153° (m. p. 151°: Werner and Skiba, Abstr., 1899, i, 190). *m*-Nitrobenzaldehyde and hydroxylamine react in alkaline solution, forming *m*-nitrobenzaldoxime melting at 123° (121°: Diamician and Silber, Abstr., 1904, i, 161; 119°: Gabriel, Abstr., 1883, 81, 919).  
G. Y.

**Action of Benzylamine on Ethyl  $\alpha$ -Crotonate.** GIOVANNI ARTINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 645—646).—The *benzylamide* of *benzylaminobutyric acid*,



prepared by heating ethyl  $\alpha$ -crotonate (1 mol.) and benzylamine (2 mols.) with absolute alcohol in a sealed tube at 150°, separates from ether in shining, well-developed, rhombic crystals [ARTINI:  $a:b:c = 1.1113:1:0.4774$ ], melts at 115—116°, and is soluble in alcohol.  
T. H. P.

**Reaction between  $\beta$ -Naphthol, Formaldehyde, and Hydroxylamine.** MARIO BETTI (*Gazzetta*, 1906, 36, i, 388—401. Compare Abstr., 1904, i, 581).—The action of formaldehyde and hydroxylamine on an alcoholic solution of  $\beta$ -naphthol yields a *compound*,



which crystallises from alcohol in mammillary masses of slender, white needles, melting and decomposing at 149°, and dissolves in benzene,

chloroform, or dilute sodium hydroxide solution, and sparingly in light petroleum; the cold alcoholic solution gives an intense reddish-brown coloration with aqueous ferric chloride. If the reaction proceeds in neutral or alkaline solution, the above compound is accompanied by methylenedinitrophenol.

In alcoholic solution, the compound melting at  $149^{\circ}$  is transformed slowly in the cold and more rapidly on boiling, into *di-β-naphtholmethylenedihydroxylamine*,  $\text{OH}\cdot\text{N}(\text{CH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH})_2$ , which crystallises from alcohol in shining, straw-yellow rhombohedra melting and decomposing at  $227^{\circ}$ , and dissolves sparingly in all organic solvents. On boiling with 20 per cent. hydrochloric acid, the compound melting at  $149^{\circ}$  is converted into *di-β-naphtholmethylenedihydroxylamine hydrochloride*,  $\text{C}_{22}\text{H}_{19}\text{O}_3\text{N}\cdot\text{HCl}$ , which forms a crystalline powder with an ill-defined melting point above  $200^{\circ}$ .

By treating with sodium hydroxide solution and subsequently saturating the liquid with carbon dioxide, the compound is converted into methylenedi-β-naphthol and di-β-naphtholmethylenedihydroxylamine.

The *acetyl* derivative,  $\text{OAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{N}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{CH}_2 \end{smallmatrix}$ , crystallises from alcohol in shining prisms melting at  $130^{\circ}$ , and exhibits normal cryoscopic behaviour in acetic acid solution.

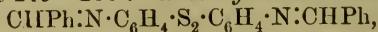
*Dibenzoyl-β-naphtholmethylenedihydroxylamine*,  $\text{OBz}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NBz}\cdot\text{OH}$ , prepared by the action of benzoyl chloride on the compound melting at  $149^{\circ}$ , dissolved in sodium hydroxide solution, separates from a mixture of alcohol and benzene in highly refractive, shining rhombohedra melting at  $177^{\circ}$ .

*β-Naphtholmethyleneamine*,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NH}_2$ , obtained by reducing the crude compound melting at  $149^{\circ}$  by means of zinc dust and hydrochloric acid, crystallises from light petroleum in colourless needles melting at  $115\text{--}116^{\circ}$  and reddens and oxidises slowly in the air, and more rapidly in a faintly alkaline solution. The *hydrochloride*,  $\text{C}_{11}\text{H}_{11}\text{ON}\cdot\text{HCl}$ , crystallises from a mixture of alcohol and hydrochloric acid in white needles melting and decomposing at  $226\text{--}227^{\circ}$ .

*Di-β-naphtholmethyleneamine*,  $\text{NH}(\text{CH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH})_2$ , also obtained by reducing the crude compound melting at  $149^{\circ}$ , crystallises from aqueous alcohol in white, prismatic needles melting at  $163^{\circ}$ . The *hydrochloride*,  $\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}\cdot\text{HCl}$ , separates from alcohol, acidified with hydrochloric acid, in colourless, rhombohedral crystals melting and decomposing at  $220^{\circ}$ .

T. H. P.

**Isomerism of *ar*-Thio-compounds.** OSCAR HINSBERG (*Ber* 1906, 39, 2427—2436. Compare *Abstr.*, 1905, i, 518).—The dithioaniline melting at  $76\text{--}77^{\circ}$  is now found to be identical with Schmidt's 4:4'-dithioaniline melting at  $78\text{--}79^{\circ}$  (m. p.  $80^{\circ}$ ; Hofmann, *Abstr.* 1895, i, 132). It forms two acetyl derivatives: that melting at  $182^{\circ}$  is labile, and changes slowly at the ordinary temperature into the stable acetate melting at  $215\text{--}216^{\circ}$ . *Dibenzylidenedithioaniline*,



is obtained in only one modification, which crystallises from alcohol in yellow needles, melts at  $136^{\circ}$ , and yields benzaldehyde when treated with dilute mineral acids.

The reduction of 4:4'-dithioaniline with zinc dust and hydrochloric acid leads to the formation of a solution containing *p*-aminophenyl mercaptan, which is oxidised on exposure to air, forming 4:4'-dithioaniline, and, on addition of acetic acid, separates as an oil; this has an unpleasant odour and is soluble in mineral acids or aqueous alkali hydroxides.

*p*-Acetylaminophenyl mercaptan,  $\text{SH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$  (Hofmann, Abstr., 1894, i, 87), is obtained on boiling 4:4'-dithioacetanilide with aluminium powder and acetic acid as a mixture of two modifications, crystallising in small, yellow leaflets. The colourless form obtained on adding hydrochloric acid to a cold alkaline solution of the mixture crystallises in white scales, commences to sinter at about  $145^{\circ}$ , melts at  $154^{\circ}$ , has in aqueous solution a slight mercaptan odour, and reddens litmus. With lead acetate, it gives a chocolate-brown, with silver nitrate a yellow precipitate, and is oxidised by air to 4:4'-dithioacetanilide melting at  $215\text{--}216^{\circ}$ , or by ferric chloride and a small quantity of hydrochloric acid to a mixture of the two isomerides melting at  $160\text{--}215^{\circ}$ . The yellow modification of *p*-acetylaminophenyl mercaptan is obtained on cooling the hot saturated aqueous solution of the mixture to  $70^{\circ}$ ; it forms yellowish-red leaflets or flat prisms and melts at  $154^{\circ}$ . Dilute solutions or concentrated solutions below  $70^{\circ}$  deposit the colourless modification. The conversion of the colourless into the yellow form takes place also slowly at  $100\text{--}137^{\circ}$  on exposure to sunlight, or quickly on crystallisation from methyl or ethyl alcohol.

*p*-Acetylaminophenyl methyl thioether,  $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , is formed by treating the lead or silver salt with methyl iodide at the ordinary temperature, by heating the mercaptan with methyl iodide and sodium hydroxide in alcohol solution, by heating the sodium mercaptide with potassium methyl sulphate and methyl alcohol at  $170^{\circ}$ , or by the action of methyl iodide on the mercaptan in pyridine solution. It crystallises in colourless leaflets or thin needles, melts at  $128^{\circ}$ , and is readily soluble in alcohol, ether, or glacial acetic acid.

*Diacetyl-p-aminophenyl mercaptan*,  $\text{SAc}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , formed by the action of acetic anhydride on the aminomercaptan in aqueous sodium hydroxide solution, crystallises in colourless leaflets and melts at  $144^{\circ}$ .

*Dithiobenzanilide*,  $\text{NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHBz}$ , formed by heating dithioaniline with benzoic anhydride, is obtained as a colourless, crystalline powder melting at  $264^{\circ}$ . When heated with aluminium powder, glacial acetic acid, and a small amount of concentrated hydrochloric acid, it yields a mixture of two *p*-benzoylaminophenyl mercaptans. The colourless modification,  $\text{NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ , is obtained by adding hydrochloric acid to the cold alkaline solution of the mixture; it crystallises in small leaflets, commences to sinter at  $165^{\circ}$ , melts at  $180^{\circ}$ , gives precipitates with lead acetate and silver nitrate, and on oxidation with ferric chloride or potassium ferrocyanide and sodium hydroxide yields dithiobenzanilide. The yellow modification, obtained by heating the colourless form or by crystallising it from alcohol,



forms large, yellow needles and melts at 182°. Both modifications form colourless solutions.

The structure of these isomeric modifications of the acylamino-phenyl mercaptans is discussed. G. Y.

**Conversion of  $\alpha$ -Nitro- $\beta$ -phenyl- $\alpha$ -methylcarbamide into  $s$ -Nitrophenylmethylcarbamide.** ROLAND SCHOLL and B. NYBERG (*Ber.*, 1906, 39, 2491—2494. Compare Scholl and Holdermann, *Annalen*, 1906, 345, 382).—The additive compound obtained from methylnitroamine and phenylcarbimide has the formula  $\text{NHPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{NO}_2$ , for by treatment at 0° with concentrated sulphuric acid a mixture of  $s$ -o-nitrophenylmethylcarbamide and  $p$ -nitrophenylmethylcarbamide is obtained, and is separated by hot 1 per cent. sodium hydroxide solution, in which the former compound is more easily soluble. The orientation of the  $\text{NO}_2$  group is determined by heating the compounds with hydrochloric acid at 120—130°, whereby  $o$ - and  $p$ -nitroaniline respectively are obtained.

$\alpha$ -Nitro- $\beta$ -phenyl- $\alpha$ -methylcarbamide yields with phenol at 100° *phenyl phenylcarbamate*, which forms colourless needles and melts at 125.5°; with aniline, it forms  $s$ -diphenylcarbamide. C. S.

**Unsaturated Disulphides.** EMIL FROMM (*Annalen*, 1906, 348, 144—160. Compare Abstr., 1895, i, 605; Hantzsch and Wolvekamp, Abstr., 1904, i, 718).—Disulphides which are decomposed with separation of sulphur on heating or on treatment with water, alkalis, ammonia, or amines, contain the grouping  $-\ddot{\text{C}}\cdot\text{S}\cdot\text{S}\cdot\ddot{\text{C}}-$ , and are not necessarily cyclic disulphides. The double linkings may connect the carbon atoms with similar atoms or groups, as in ethyl dioxothiocarbonate,  $\text{S}\cdot\text{C}(\text{OEt})\cdot\text{S}\cdot\text{S}\cdot\text{C}(\text{OEt})\cdot\text{S}$ , dibenzoyl sulphide,  $\text{O}\cdot\text{CPh}\cdot\text{S}\cdot\text{S}\cdot\text{CPh}\cdot\text{O}$ , or phenylthiouret,  $\text{NH}\langle\begin{smallmatrix} \text{C}(\text{NPh}) \\ \text{C}(\text{NH}) \end{smallmatrix}\rangle\text{S}_2$ , or with dissimilar atoms or groups, as in perthiocyanic acid,  $\text{NH}\langle\begin{smallmatrix} \text{C}(\text{NH}) \\ \text{C}(\text{S}) \end{smallmatrix}\rangle\text{S}_2$ . The reaction is often complicated by the interaction of the primary products. If the double linkings are part of stable ring systems, as in diphenyl disulphide,  $\text{SPh}\cdot\text{SPh}$ , or the thiodiazolone disulphides (Busch, Abstr., 1896, i, 190), the decomposition by means of alkalis takes place, but without separation of sulphur. Disulphides which do not contain the above grouping are stable towards alkalis.

The author discusses the constitution of the sulphides and oxides of the thiocarbimides which, as represented by Freund (Abstr., 1895, i, 576), form exceptions to this rule. G. Y.

**Dithiobiurets.** EMIL FROMM and KURT SCHNEIDER (*Annalen*, 1906, 348, 161—174. Compare Fromm, Abstr., 1893, i, 575).—Perthiocyanic acid reacts with  $p$ -toluidine,  $o$ -toluidine,  $as$ - $m$ -xylidine, and  $o$ -phenetidine, forming the thiobiurets, thiocarbamides, and sulphur. The dithiobiurets, which are isolated by extraction with cold dilute alkali hydroxides, are oxidised by iodine, forming the thiourets, which are bases, and when heated with concentrated hydrochloric acid at 165° yield 2-aminobenzothiazoles.

*p*-Tolyldithiobiuret melts at  $173\cdot5^{\circ}$  ( $159^{\circ}$ ; Tursini, Abstr., 1884, 1140) and forms *p*-tolylthioureth hydriodide,  $\text{NH} \begin{array}{c} \text{C}(\text{N}\cdot\text{C}_7\text{H}_7)\cdot\text{S} \\ \text{C}(\text{NH})\text{-----S} \end{array} \text{HI}$ , separating in yellow crystals and melting at  $221\cdot5^{\circ}$ . Contrary to Tursini's statement (*loc. cit.*), *p*-tolyldithiobiuret reacts with 1 mol. of methyl iodide to form *methyl-p-tolyl-ψ-dithiobiuret*,  $\text{C}_{10}\text{H}_{13}\text{N}_3\text{S}_2$ , which crystallises in nodular aggregates of needles and melts at  $125\cdot5^{\circ}$ . With 2 mols. of methyl iodide, it forms *dimethyl-p-tolyl-ψ-dithiobiuret*,  $\text{C}_7\text{H}_7\cdot\text{N}:\text{C}(\text{SMe})\cdot\text{NH}\cdot\text{C}(\text{SMe})\cdot\text{NH}$ , which crystallises in white needles, melts at  $67^{\circ}$ , and evolves mercaptan at  $100^{\circ}$ . When treated with acetone and hydrogen chloride, this forms *methyl-p-tolyldimethyl-ψ-dithioketuret*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:\text{C}(\text{SMe})\cdot\text{N} \begin{array}{c} \text{C}(\text{SMe}) \\ \text{CMe}_2 \end{array} \text{N}$ , which crystallises in white needles and melts and decomposes at  $164^{\circ}$ . *p*-Tolyl-ψ-thiobenzylcyanocarbamide,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{C}(\text{SC}_7\text{H}_7):\text{N}\cdot\text{CN}$ , prepared by heating *p*-tolyldithiobiuret with sodium hydroxide and benzyl chloride in alcoholic solution, crystallises in glistening, white scales and melts at  $181\cdot5^{\circ}$ .

*o*-Tolyldithiobiuret,  $\text{C}_9\text{H}_{11}\text{N}_3\text{S}_2$ , crystallises in stout needles and melts at  $159^{\circ}$ . *o*-Tolylthioureth hydriodide,  $\text{C}_9\text{H}_9\text{N}_3\text{S}_2\cdot\text{HI}\cdot\text{C}_2\text{H}_6\text{O}$ , crystallises from alcohol in yellow needles and melts at  $153^{\circ}$ . *o*-Tolyl-ψ-thiobenzylcyanocarbamide,  $\text{C}_{10}\text{H}_{16}\text{N}_3\text{S}$ , forms a white, crystalline powder and melts at  $165^{\circ}$ .

*m*-Xylyldithiobiuret,  $\text{C}_{10}\text{H}_{13}\text{N}_3\text{S}_2$ , forms yellow crystals and melts at about  $129^{\circ}$ . *m*-Xylylthioureth hydriodide,  $\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}_2\cdot\text{HI}$ , crystallises in yellow needles and melts at  $146^{\circ}$ .

*o*-Methoxyphenyldithiobiuret,  $\text{C}_{10}\text{H}_{13}\text{ON}_3\text{S}_2$ , forms long, yellow needles and melts at  $153^{\circ}$ . *o*-Methoxyphenylthioureth hydriodide,



forms stout, yellow needles and melts at  $181\text{--}182^{\circ}$ ; the *hydrochloride* forms yellow needles and melts at  $205^{\circ}$ . G. Y.

**Action of Alkali Hydroxides and Alkyl oxides on Unsaturated Imides.** ARNALDO PIUTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 79—87).—The violet coloration given by *p*-methoxyphenylcitraconimide and other analogous imides (Abstr., 1889, 590) depends on the formation of an additive compound of the alkali or alkaline-earth hydroxide or their alkyl oxides or acetates with the imide itself, a compound which is transformed by moisture into a salt of *p*-methoxyphenylcitraconic acid.

T. H. P.

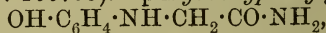
**Preparation of Phenols and their Substitution Products.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 167211).—The replacement of a diazonium complex by a hydroxyl group is a reaction which does not always proceed smoothly, and the following process has been found to give favourable results. The solutions of the diazonium salts derived from *o*-anisidine, *o*- and *p*-aminophenols, and *o*-toluidine are introduced into a boiling 50 per cent. solution of copper sulphate. The guaiacol and *o*-cresol produced from *o*-anisidine and *o*-toluidine respectively are distilled in steam, whilst the catechol and quinol

obtained from the aminophenols are extracted with ether. From 1.2 to 5 parts of copper sulphate are employed to one of the aromatic amine. G. T. M.

**Behaviour of Trinitrobenzene Derivatives with Cyclic Amines.** E. O. SOMMERHOFF (*Zeit. Farb. Ind.*, 1906, 5, 270—271).—In connection with von Georgievics' view that picric acid is capable of existing in two differently coloured forms (this vol., i, 420), it is pointed out that on moistening picric acid with aniline a red colour is first developed which changes to yellow as the ordinary picrate is formed. With dimethylamine in alcoholic solution, picric acid gives the yellow picrate at once, but in benzene solution a transient red coloration is observed. The additive compounds described in conjunction with Noelting (this vol., i, 157) are referred to, and the author is led to dissent from von Georgievics' theoretical views. W. A. D.

***p*-Aminodiphenyl Oxide-3-sulphonic Acid.** AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 169357).—When *p*-aminodiphenyl oxide is sulphonated with concentrated sulphuric acid at 80—100°, a sulphonic acid is produced containing the sulpho-group in the unsubstituted ring, but when the acid sulphate of *p*-aminodiphenyl oxide is baked at 180° the sulpho-group enters an ortho-position with respect to the amino-group. The new *p*-aminodiphenyl oxide 3-sulphonic acid yields valuable lake-forming azo-colouring matters; the free acid and its sodium, calcium, and copper salts are only sparingly soluble in water. G. T. M.

***p*-Hydroxyphenylglycinamide.** AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 166799).—*p*-Hydroxyphenylglycinamide,



is obtained by condensing chloroacetamide with *p*-aminophenol in the presence of substances capable of fixing hydrogen chloride; an excess of *p*-aminophenol would answer this purpose. For use as a photographic developer, the *p*-hydroxyphenylglycinamide is dissolved in 200 parts of water containing 5 parts of potassium carbonate and 5 parts of anhydrous sodium sulphite. G. T. M.

**Derivatives of 3-Amino-*p*-cresol-5-sulphonic Acid.** KALLE & Co. (D.R.-P. 168857).—3-Amino-*p*-cresol-5-sulphonic acid is readily acetylated when dissolved in water and the solution exactly neutralised, and the acetyl derivative when nitrated below 5° with a mixture of concentrated nitric and sulphuric acids yields a well-defined, crystalline nitro-derivative, which is readily hydrolysed on boiling with hydrochloric acid. The nitro-3-amino-*p*-cresol-5-sulphonic acid which is thus obtained in a crystalline condition furnishes an azo- $\beta$ -naphthol having valuable tinctorial properties. G. T. M.

**Preparation of 3-Amino-2-hydroxybenzylamine.** ALFRED EINHORN (D.R.-P. 167572).—3-Nitro-2-hydroxybenzylamine, when reduced with tin and hydrochloric acid, furnishes 3-amino-2-hydroxybenzylamine; this substance, which is a valuable photographic developer,



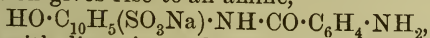
may also be prepared by reducing benzoyl-3-nitro-2-hydroxybenzylamine to *ω*-benzoyl-3-amino-2-hydroxybenzylamine, a base which crystallises in colourless needles melting at 186°, and then hydrolysing this product with concentrated hydrochloric acid. 3-Amino-2-hydroxybenzylamine furnishes a soluble dihydrochloride crystallising in colourless needles; it develops a violet coloration with ferric chloride, precipitates silver from Tollens' solution, sets free gold from its salts, giving rise to a violet coloration, and forms crystalline platini- and stanni-chlorides.

G. T. M.

**Preparation of 4-Chloro-*α*-naphthol.** KALLE & Co. (D.R.-P. 167458).—*α*-Naphthol is conveniently chlorinated by slowly adding to its cold alkaline solution one molecular proportion of sodium hypochlorite also dissolved in aqueous sodium hydroxide. The addition of dilute acetic or hydrochloric acid liberates 4-chloro-*α*-naphthol, which first separates as an oil and then solidifies in aggregates of needles. The product after distillation in superheated steam or crystallisation in light petroleum melts at 64–65°, and the yield is extremely good.

G. T. M.

**Preparation of Aminoarylacylaminonaphtholsulphonic Acids.** GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 170045).—The aminonaphtholsulphonic acids readily react in aqueous solution at moderate temperatures with the chlorides of the nitro- and acetyl-amino-acids of the aromatic series. Thus sodium 6-amino-*α*-naphthol-3-sulphonate condenses with *m*-nitrobenzoyl chloride in neutral aqueous solution in the presence of sodium acetate to form the compound  $\text{HO} \cdot \text{C}_{10}\text{H}_5(\text{SO}_3\text{Na}) \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , and this substance on reduction gives rise to an amine,



which combines with diazonium salts to produce azo-colouring matters capable of being again diazotised and condensed on the fibre. Similarly, sodium 6-amino-*α*-naphthol-3-sulphonate combines with acetylaminobenzoyl and benzenesulphonic chlorides, and the products when hydrolysed also give rise to aminosulphonic acids which are used in the production of ingrain azo-dyes.

G. T. M.

**Condensation Products of *α*-Naphthol and Benzophenone Chloride.** ALBERT G. SHRIMPTON (*Chem. News*, 1906, 94, 13–14. Compare McKenzie, *Trans.*, 1896, 69, 985; 1901, 79, 1204).—Diphenyldihydroxydi-*α*-naphthylmethane,  $\text{CPh}_2(\text{C}_{10}\text{H}_6 \cdot \text{OH})_2$ , obtained when benzophenone chloride is heated with *α*-naphthol, forms microscopic crystals which darken at 204°, and ultimately melt to a brown, viscid liquid at 208.2–209.2°. When heated with sodium acetate and acetic anhydride in a reflux apparatus, it yields small, silky-white needles and plates melting at 202°, of uncertain composition. When the reaction between *α*-naphthol and benzophenone chloride is moderated by the presence of a considerable amount of light petroleum, a product is obtained which, when recrystallised from acetone, forms slender, yellow, microscopic prisms melting at 180.5–181°.

D. A. I.

**Diisoapiole, Diisoeugenol Methyl Ether, and Diasarone.** TIBOR SZÉKI (*Ber.*, 1906, **39**, 2422—2424. Compare Tiemann, *Abstr.*, 1892, 45; Angeli and Mola, *Abstr.*, 1895, i, 24).—*Diisoapiole*,  $C_{24}H_{28}O_8$ , prepared by treating *isoapiole* with hydrogen chloride in ethereal solution, evaporating off the ether, and heating the residual oil at  $200^\circ$  in a sealed tube, forms white crystals and melts at  $97^\circ$ .

*Diisoeugenol methyl ether*,  $C_{22}H_{28}O_4$ , formed by the action of hydrogen chloride on *isoeugenol methyl ether* in ethereal solution, crystallises in snow-white, glistening needles and melts at  $106^\circ$ .

*Diasarone*,  $C_{24}H_{32}O_6$ , formed in the same way from *asarone*, crystallises from alcohol in white needles and melts at  $100^\circ$ .

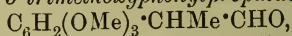
These three polymerisation products are readily soluble in the usual solvents, and do not form additive compounds with bromine.

In one experiment the diasarone was accompanied by *s-di-trimethoxyphenylethylene*,  $C_2H_2[C_6H_2(OMe)_3]_2$ , which forms white crystals, melts at  $96^\circ$ , and forms an *additive* compound with bromine.

G. Y.

**Derivatives of Asarone.** TIBOR SZÉKI (*Ber.*, 1906, **39**, 2419—2421).—*Dihydroasarone*,  $C_6H_2Pr^a(OMe)_3$ , prepared by reducing asarone with sodium in alcoholic solution, is obtained as an aromatic, colourless oil, which boils at  $185$ — $188^\circ$  under 40 mm. pressure, and is miscible with alcohol, ether, benzene, or glacial acetic acid.

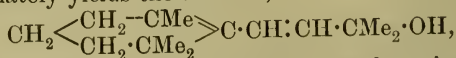
Asarone dibromide (Rizza and Butleroff, *Abstr.*, 1884, 1042), prepared by the action of bromine on asarone in carbon disulphide solution, melts at  $83^\circ$ , and when boiled with sodium ethoxide in alcoholic solution, yields an impure oil having an unpleasant odour. When treated with mercuric oxide and iodine in cooled alcoholic solution, asarone yields  $\alpha$ -2:4:5-trimethoxyphenylpropaldehyde,



which is an oil boiling at  $275^\circ$  under the ordinary pressure.

G. Y.

**Preparation of Tertiary Alcohols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 166898, 166899).—By the action of excess of organic magnesium haloids ( $MgRBr, Et_2O$ ) on the carboxylic acids or their metallic salts, additive products are obtained, which on treatment with water or acid give rise to a tertiary alcohol. Thus the ethereal solutions of magnesium ethyl bromide and benzoic acid when slowly mixed in the cold evolve ethane and give a precipitate which dissolves completely in dilute ice-cold sulphuric acid. The ethereal extract of this solution furnishes phenyldiethylcarbinol,  $CEt_2Ph \cdot OH$ , which boils at  $110^\circ$  under 12 mm. pressure. *cyclo*Citrylideneacetic acid, when treated in this way with magnesium methyl bromide, ultimately yields the *carbinol*,

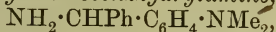


which boils at  $130^\circ$  under 12 mm. pressure; methane is evolved during the initial stage of the reaction. In this operation dry sodium *cyclo*-citrylideneacetate may be substituted for the free acid, and in a similar manner anhydrous sodium benzoate may be employed in the preparation of phenyldiethylcarbinol.

G. T. M.

**Preparation of *p*-Dialkylaminobenzhydrylamines.** EMANUEL MERCK (D.R.-P. 167053).—The oximes, phenylhydrazones, and semicarbazides of the *p*-dialkylaminobenzophenones ( $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2$ ), when reduced electrically or in neutral acid or alkaline solution with the help of sodium or sodium amalgam, give rise to the *p*-dialkylaminobenzhydrylamines.

*p*-Dimethylaminobenzophenoneoxime crystallises in colourless prisms melting at  $152\text{--}154^\circ$ , and when reduced with sodium and ethyl alcohol yields *p*-dimethylaminobenzhydrylamine,



which forms colourless, acicular crystals and melts at  $82\cdot5^\circ$ ; the hydrochloride separates in sparingly soluble leaflets melting at  $186\text{--}187^\circ$ .

*p*-Diethylaminobenzophenoneoxime crystallises in colourless needles melting at  $175\text{--}177^\circ$ ; the corresponding hydrazone is oily.

*p*-Diethylaminobenzhydrylamine,  $\text{NH}_2\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}_2$ , separates in colourless needles melting at  $120\text{--}121^\circ$ ; its hydrochloride, which is obtained in voluminous aggregates of needles, is sparingly soluble in cold water. These dialkylaminobenzhydrylamines form a new class of anæsthetics.

G. T. M.

**Preparation of *p*-Dialkylaminobenzhydrylamines.** EMANUEL MERCK (D.R.-P. 167462, 167463).—Dimethylaminobenzhydrylamine may be obtained by heating either dimethylaminobenzhydrol, the ethyl ether of this substance, or diethylaminodiphenylbromomethane with ammonia under pressure at  $150\text{--}200^\circ$ ; it can also be prepared by heating the last of these three compounds with potassium phthalimide at  $180^\circ$ , and then eliminating phthalic acid from the intermediate product by digestion in an autoclave with aqueous alcoholic ammonia at  $140^\circ$ .

G. T. M.

**Reduction of Aromatic Carbinols.** AUGUST KLAGES (*Ber.*, 1906, 39, 2587—2595).—[With ERNST LAUCK and KARL GIESER.]—The reduction of cinnamyl alcohol by sodium and alcohol yields a mixture of propenylbenzene,  $\text{CHPh}\cdot\text{CHMe}$ , and propylbenzene; the former compound was identified by oxidising it to benzoic acid.  $\alpha$ -Phenylallyl alcohol (this vol., i, 638), with the same reducing agent, yields a mixture of allylbenzene and propylbenzene, which, after treatment with alcoholic potash at  $130^\circ$ , contains propenylbenzene, identified in the form of its bromide.

$\alpha$ -Phenyl- $\Delta^{\alpha}$ -butene- $\gamma$ -ol is conveniently obtained by decomposing the reaction product of magnesium methyl bromide and cinnamaldehyde with an ice-cold solution of ammonium chloride. It boils at  $131^\circ$  under 12 mm. pressure, and by reduction with sodium and alcohol yields a mixture of butylbenzene and  $\alpha$ -phenyl- $\Delta^{\beta}$ -butylene.

$\alpha$ -Phenyl- $\Delta^{\alpha}$ -pentene- $\gamma$ -ol,  $\text{CHPh}\cdot\text{CH}\cdot\text{CHEt}\cdot\text{OH}$ , obtained like the preceding alcohol from magnesium ethyl bromide, is a colourless oil which boils at  $138^\circ$  under 11·5 mm. pressure, and is reduced by sodium and alcohol to  $\alpha$ -phenyl- $\Delta^{\beta}$ -pentene,  $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CHEt}$ , a colourless, mobile oil with a peculiar odour, which boils at  $80^\circ$  under 12 mm. pressure, has a sp. gr.  $0\cdot8837$  at  $16^\circ/4^\circ$ ;  $n_D$   $1\cdot5059$  at  $16^\circ$ , and



forms an oily *bromide*,  $C_{11}H_{14}Br_2$ . When this hydrocarbon is heated with alcoholic potash at  $150^\circ$  for one day it is changed into  $\alpha$ -phenyl- $\Delta^{\alpha}$ -pentene,  $CHPh:CHPr^a$ , which boils at  $82^\circ$  under 9 mm. pressure, has a sp. gr.  $0.892$  at  $15^\circ/4^\circ$ ,  $n_D$   $1.5139$  at  $15^\circ$ , and forms a *bromide*,  $C_{11}H_{14}Br_2$ , which separates from alcohol in colourless leaflets and melts at  $61^\circ$ .

$\alpha$ -Phenyl- $\gamma$ -methyl- $\Delta^{\alpha}$ -butene- $\gamma$ -ol,  $CHPh:CH \cdot CMe_2 \cdot OH$ , is obtained by decomposing the reaction product of magnesium methyl bromide and benzylideneacetone with ice and ammonium chloride; it melts at  $38.5^\circ$ , boils at  $123$ — $124^\circ$  under 11 mm pressure, and is reduced by sodium and alcohol to  $\alpha$ -phenyl- $\gamma$ -methyl- $\Delta^{\beta}$ -butylene (Abstr., 1904, i, 569).

$\alpha$ -Phenyl- $\gamma$ -methyl- $\Delta^{\alpha}$ -pentene- $\gamma$ -ol,  $CHPh:CH \cdot CMeEt \cdot OH$ , obtained like the preceding alcohol from magnesium ethyl bromide, boils at  $124$ — $125^\circ$  under 11 mm. pressure, and is not reduced by sodium and alcohol.

$\alpha$ -Phenyl- $\gamma$ -methyl- $\Delta^{\alpha}$ -pentadiene,  $CHPh:CH \cdot CMe:CHMe$ , obtained by decomposing the reaction product of magnesium ethyl iodide (2 mols.) and benzylideneacetone (1 mol.) with ice and dilute sulphuric acid, boils at  $130^\circ$  under 20 mm. pressure, has a sp. gr.  $0.9593$  at  $19^\circ/4^\circ$ ,  $n_D$   $1.5366$ , and is reduced by sodium and alcohol to  $\alpha$ -phenyl- $\gamma$ -methyl- $\Delta^{\beta}$ -pentene,  $CH_2Ph:CH:CMeEt$ , a colourless, mobile oil which boils at  $119$ — $120^\circ$  under 20 mm. and at  $226^\circ$  under 749 mm. pressure, has a sp. gr.  $0.9014$  at  $18^\circ/4^\circ$ ,  $n_D$   $1.5100$ , and forms a *nitrosylchloride*, which melts at  $151^\circ$ .

Carbinols of the type  $CPh:C \cdot CHR \cdot OH$  (where  $R$ =alkyl) are obtained from magnesium alkyl haloids and either phenylpropargylaldehyde or  $\alpha$ -bromocinnamaldehyde; in the latter case the intermediate brominated alcohol must be boiled with alcoholic potash.

$\alpha$ -Phenyl- $\alpha$ -butinene- $\gamma$ -ol,  $CPh:C \cdot CHMe \cdot OH$ , obtained by the second method, is a colourless oil which boils at  $121$ — $122^\circ$  under 9 mm. pressure, and is reduced by sodium and alcohol to a mixture of  $\Delta^{\beta}$ -butenylbenzene and a small quantity of butylbenzene.

$\alpha$ -Phenyl- $\alpha$ -pentinene- $\gamma$ -ol,  $CPh:C \cdot CHEt \cdot OH$ , obtained by the first method, boils at  $133$ — $134^\circ$  under 10.5 mm. pressure, has a sp. gr.  $1.018$  at  $15.5^\circ/4^\circ$ ,  $n_D$   $1.5570$  at  $15.5^\circ$ , and forms a heavy oily *bromide*,  $C_{11}H_{12}Br_2$ , with hydrogen bromide in glacial acetic acid. When the acetylenic alcohol is prepared by the second method, the intermediate  $\beta$ -bromo- $\alpha$ -phenyl- $\Delta^{\alpha}$ -pentene- $\gamma$ -ol,  $CHPh:CBr \cdot CHEt \cdot OH$ , boils at  $146$ — $147^\circ$  under 11 mm. pressure, has a sp. gr.  $1.3533$  at  $17^\circ/4^\circ$ , and  $n_D$   $1.5840$  at  $17^\circ$ . The reduction of the acetylenic alcohol by sodium and alcohol yields the  $\Delta^{\beta}$ -pentenylbenzene described above. C. S.

**Migration of the Phenyl Group in the Halohydrins and the  $\alpha$ -Glycols.** MARC TIFFENEAU (*Compt. rend.*, 1906, 142, 1537—1539. Compare Abstr., 1902, i, 666; 1904, i, 63, 133).— $\beta\beta$ -Diphenylethylene glycol,  $OH \cdot CPh_2 \cdot CH_2OH$ , prepared by the action of magnesium phenyl bromide on ethyl glycollate, is converted quantitatively into diphenylacetaldehyde,  $CHPh_2 \cdot CHO$ , by the action of sulphuric acid, and  $\alpha$ -phenylpropylene- $\alpha\beta$ -glycol,  $OH \cdot CHPh \cdot CHMe \cdot OH$  (compare

Zincke, Abstr., 1884, 1003), is converted similarly into phenylacetone,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_3$ .

The transformation of the substituted  $\alpha$ -glycols into the corresponding aldehyde or ketone by the action of sulphuric acid does not therefore involve the migration of a phenyl group except in the case of hydrobenzoin, whilst in the similar transformation of the corresponding iodohydrins by means of silver nitrate the change is always accompanied by the migration of a phenyl group. M. A. W.

**Cholesterol. II. Specific Rotations of Cholestene and Cholestane Derivatives.** JULIUS MAUTHNER (*Monatsh.*, 1906, 27, 421—431. Compare this vol., i, 579; Mauthner and Suida, Abstr., 1894, i, 326, 486; 1896, i, 425; 1897, i, 31; 1903, i, 625; Windaus, Abstr., 1904, i, 49, 667; this vol., i, 174, 579, 580; Diels and Abderhalden, this vol., i, 272).—The author has determined the influence of the addition of halogens and of hydrogen haloids on the specific rotations of cholesterol, cholestene, and cholestane. The substances were dissolved in ether, alcohol, or chloroform.

Cholesterol has  $[\alpha]_D - 29.92^\circ$ , the hydrochloride  $[\alpha]_D + 5.7^\circ$ , the dichloride  $[\alpha]_D - 29.1^\circ$ , and the dibromide  $[\alpha]_D - 41.6^\circ$ . Cholestanonol has  $[\alpha]_D - 3.14^\circ$ .

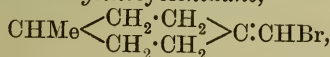
Cholesteryl acetate has  $[\alpha]_D - 29.8^\circ$ , its dichloride  $[\alpha]_D - 32.8^\circ$ , and its dibromide  $[\alpha]_D - 45.1^\circ$ .

Cholesteryl chloride has  $[\alpha]_D - 26.36^\circ$ ; the hydrochloride [ $\beta$ -dichlorocholestane] has  $[\alpha]_D + 20.1^\circ$  in benzene solution or  $+ 12.16^\circ$  in ethereal solution. Trichlorocholestane has  $[\alpha]_D - 34.7^\circ$ . Cholesteryl chloride dibromide, which melts at  $130\text{—}131^\circ$ , has  $[\alpha]_D - 55.0^\circ$ .

Cholestene hydrochloride [chlorocholestane] has  $[\alpha]_D + 21.8^\circ$ , and cholestene dichloride [ $\alpha$ -dichlorocholestane]  $[\alpha]_D - 28.7^\circ$ .

$\alpha$ -Cholestene dibromide (Mauthner and Suida, Abstr., 1894, i, 326) melts at  $145\text{—}146^\circ$  and has  $[\alpha]_D + 48.9^\circ$ .  $\beta$ -Cholestene dibromide immediately after solution in chloroform has  $[\alpha]_D - 39.6^\circ$ , after twenty-four hours  $[\alpha]_D \pm 0^\circ$ , and at the end of some days  $[\alpha]_D + 39.4^\circ$ . The last specific rotation is not increased beyond  $+ 40^\circ$  on heating the solution in a sealed tube at  $65^\circ$  for one hour, but on evaporation the  $\alpha$ -dibromide is obtained. The change in the rotation takes place much more slowly in benzene solution. The dibromocholestanes are probably alicyclic *cis-trans*-isomerides. G. Y.

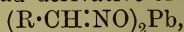
**4-Methylcyclohexylidene-1-acetic Acid.** WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, 39, 2404—2405. Compare this vol., i, 360, 584).—When treated with bromine in aqueous sodium carbonate solution, 4-methylcyclohexylidene-1-acetic acid, melting at  $40.5\text{—}41^\circ$ , yields 1-methyl-4-bromomethylenecyclohexane,



which, when heated with water at  $140\text{—}150^\circ$ , forms hexahydro-*p*-tolu-aldehyde (Wallach and Evans, this vol., i, 566). Perkin and Pope's acid melting at  $28^\circ$  (Proc., 1906, 22, 107) is probably 4-methyl- $\Delta^1$ -cyclohexene-1-acetic acid,  $\text{CHMe} \begin{array}{c} \text{CH}_2-\text{CH} \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (compare Rupe, Ronus, and Lotz, Abstr., 1903, i, 139). G. Y.

*See errata*  
1922, p. 1381

**Conversion of Aldoximes into Nitriles.** WALTHER BORSCH (Ber., 1906, 39, 2503).—If 2 mols. of an aldoxime are heated with 1 mol. of lead oxide, the lead derivative of the aldoxime,



is formed, and on further heating is decomposed into lead oxide, water and the nitrile. The violence of the action is moderated by mixing the reacting substances with an amount of sand two to three times the weight of the aldoxime. Nitriles have been prepared in this manner from benzaldoxime, anisaldoxime, cuminaldoxime, heptaldoxime, and furfuraldoxime. G. Y.

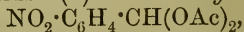
**Crystallographic Study of New Organic Compounds** FRANCESCO RANFALDI (*Atti R. Accad. Lincei*, 1906, [v], 15, i 715—724).—Sodium 2-*o*-nitro-*p*-toluidino-3:5-dinitrobenzoate (Cuttitta, *Rend. Soc. Chim. Roma*, 1905, 146) crystallises in the trichlinic system [ $a:b:c=1.52579:1.094494$ ;  $\alpha=76^\circ 11'$ ,  $\beta=81^\circ 27'$ ,  $\gamma=93^\circ 29'$ ].

The corresponding pyridine salt (Cuttitta, *loc. cit.*) crystallises in the triclinic system [ $a:b:c=1.35414:1.109430$ ;  $\alpha=87^\circ 16'$ ,  $\beta=76^\circ 36'$ ,  $\gamma=92^\circ 14'6''$ ].

*i*-Lupanine platinichloride (Soldaini, *Abstr.*, 1892, 892) crystallises in the monoclinic system [ $a:b:c=2.6124:1.13428$ ;  $\beta=83^\circ 46'33''$ ].

*Ethyl naphthalate* (Errera),  $C_{10}H_6(CO_2Et)_2$ , melting at  $58-60^\circ$  crystallises in the monoclinic system [ $a:b:c=1.0555:1.31814$ ,  $\beta=70^\circ 45'27''$ ]. T. H. P.

**Products of Dehydration of Phenyl-*o*-nitrocinnamic Acid and the Products which accompany this Acid when prepared by Perkin's Synthesis.** MARUSSIA BAKUNIN and L. PARLATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 18—34).—When sodium phenylacetate, *o*-nitrobenzaldehyde, and acetic anhydride are heated at  $120^\circ$ ,  $\alpha$ -phenyl-*o*-nitrocinnamic acid is formed and less resin is obtained than at  $160^\circ$ . The portion of the product insoluble in sodium carbonate solution contains: (1) *o*-nitrobenzylidene diacetate,



which crystallises from light petroleum in small, yellow prisms melting at  $89-90^\circ$ , dissolves in most solvents, and is slightly decomposed by a solution of phenylhydrazine, giving *o*-nitrobenzaldehyde phenylhydrazone; (2) *phenyl-o-nitrophenylacrylene* (?) [*phenyl-o-nitrophenylenethylene*],  $NO_2 \cdot C_6H_3 < \begin{smallmatrix} CH \\ | \\ CPh \end{smallmatrix}$ , which crystallises from ethyl

acetate in ruby-red, shining, rhombic laminae

$$[a:b:c=0.68275:1.104489]$$

and melts at  $186-187^\circ$ .

*Ethyl phenyl-o-nitrocinnamate*, obtained by the action of alcohol on the acid, separates from light petroleum in yellow, monoclinic prism melting at  $59^\circ$  and is soluble in alcohol.

*Phenylhydrazine phenyl-o-nitrocinnamate*,  $C_{15}H_{11}O_4N \cdot NHPh \cdot NH_2$ , crystallises from benzene in tufts of silky, yellow, unstable needle and melts at  $97-103^\circ$ .



*Phenyl-o-nitrocinnamoyl phenylhydrazide*,  $C_{21}H_{17}O_3N_3$ , prepared by the action of excess of phenylhydrazine on phenyl-*o*-nitrocinnamic anhydride, crystallises from alcohol in shining, yellow laminae melting at  $167^\circ$ . It is accompanied by a small quantity of a yellow powder, infusible at  $300^\circ$ , the nature of which has not been determined.

*Phenyl-o-nitroindone phenylhydrazone*,  $C_{15}H_9O_2N:N_2HPh$ , crystallises from benzene in canary-yellow, silky needles melting at  $135-136^\circ$ . The *oxime*,  $C_{15}H_{10}O_2N:NOH$ , crystallises from benzene in silky, orange-yellow needles melting at  $246-248^\circ$ .  
T. H. P.

**Action of Sodium Hypochlorite and of Bromine and Sodium Alkyloxides on Hydrocinnamamide.** R. A. WEERMANN and W. J. A. JONGKEES (*Rec. trav. chim.*, 1906, 25, 238—243).—Hydrocinnamamide (1 mol.) reacts with sodium hypochlorite (1 mol.) and sodium hydroxide ( $\frac{1}{2}$  mol.) at the ordinary temperature to form *s*- $\beta$ -diphenylethylcarbamide; if, however, the quantity of sodium hydroxide is increased and the temperature is raised to  $80^\circ$ ,  $\beta$ -diphenylethylamine is obtained.

Hydrocinnamamide reacts with bromine and sodium ethoxide or methoxide at the boiling point of the alcohol to form the corresponding alkyl ester of  $\beta$ -phenylethylaminoformic acid; ethyl benzylaminoformate, similarly prepared from phenylacetamide, melts at  $44^\circ$ , and *methyl benzylaminoformate* crystallises in thin needles from light petroleum and melts at  $64-65^\circ$ .  
M. A. W.

**Formation of Salicylic Acid from Sodium Phenoxide.** JACOB MOLL VAN CHARANTE (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 20—23).—On heating sodium phenyl carbonate in a sealed tube at  $100^\circ$ , carbon dioxide and phenol are formed along with small amounts of sodium salicylate. Sodium phenoxide crystallises from acetone with 1 mol. of the solvent in long, soft, and almost white needles. When sodium phenyl carbonate is placed in dry acetone, it yields carbon dioxide, phenol, and a mixture of normal and acid sodium carbonates. Sodium salicylate crystallises from acetone in small needles containing  $\frac{1}{2}$  to 1 mol. of the solvent, whereas disodium salicylate is insoluble in acetone.  
E. F. A.

**Bismuth Disalicylate.** CHEMISCHE FABRIK VON HEYDEN, AKTIEN-GESELLSCHAFT (D.R.-P. 168408).—The "*bismuthum salicylicum basicum*" or "*bismuthum subsalicylicum*" of commerce is the monosalicylate of bismuth having the formula  $OH \cdot C_6H_4 \cdot CO \cdot O \cdot BiO$ . The so-called neutral bismuth salicylate is a mixture of a basic salt and free salicylic acid. *Bismuth disalicylate*,  $OH \cdot Bi(O \cdot CO \cdot C_6H_4 \cdot OH)_2$  or  $O[Bi(O \cdot CO \cdot C_6H_4 \cdot OH)_2]_2$ , has now been prepared by adding crystallised bismuth nitrate to an aqueous solution of sodium salicylate, and, after thorough mixing, extracting the free salicylic acid at the ordinary temperature with either dilute ammonia or indifferent solvents such as alcohol, ether, or chloroform. The product is a white, almost tasteless powder, which has a neutral reaction in cold water, but is decomposed on warming into the monosalicylate and free salicylic acid.

G. T. M.

**Action of Chloroform and Sodium Hydroxide on Phenols in Acetone Solution.** GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 579—587).—The compound,  $C_{10}H_{12}O_3$ , which was obtained by Link (D.R.-P. 80986) by heating an acetone solution of phenol with chloroform and sodium hydroxide, and was regarded by this author as hydroxyphenyl hydroxyisopropyl ketone or hydroxyisobutyrylphenol,  $OH \cdot C_6H_4 \cdot CO \cdot CMe_2 \cdot OH$ , exhibits none of the reactions of phenols or ketones, whilst it contains a carboxyl group; it must hence be assumed to be  $\alpha$ -phenoxyisobutyric acid,  $OPh \cdot CMe_2 \cdot CO_2H$ , and it agrees in properties with the data given by Bischoff (Abstr., 1900, i, 345) for this compound. The corresponding naphthol derivatives described by Link are identical with the  $\alpha$ - and  $\beta$ -naphthoxyisobutyric acids prepared by Bischoff (Abstr., 1900, i, 395).

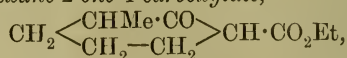
By the action of chloroform, sodium hydroxide, and acetone on *o*- or *p*-cresol or thymol, the author has obtained compounds identical with those prepared by Bischoff (Abstr., 1900, i, 392 and 394) by the action of ethyl  $\alpha$ -bromoisobutyrate on the sodium derivatives of *o*- or *m*-cresol or thymol.

The views of Link concerning these compounds (compare Beilstein, Handbuch, III, Suppl., 120 and 143) are hence erroneous.

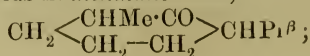
The first phase in the reaction is probably the formation of acetone-chloroform (which may, indeed, be used in place of the chloroform), this being then acted on by sodium hydroxide in presence of acetone, yielding  $\alpha$ -hydroxyisobutyric acid, which, with the phenol, gives  $\alpha$ -phenoxyisobutyric acid. The chloroform may also be replaced by bromoform, bromal, chloral, or carbon tetrachloride or tetrabromide.

The compounds prepared by the author have all been described previously. T. H. P.

**Syntheses by means of the Carboxylic Esters of Cyclic Ketones. II. Synthesis of *m*-Menthane-2-one and of *m*-Menthane-4-one from 1-Methylcyclohexane-2-one and 1-Methylcyclohexane-4-one.** ARTHUR KÖTZ and A. MICHELS (*Annalen*, 1906, 348, 91—96. Compare Kötz and Hesse, this vol., i, 88).—When distilled under reduced pressure, ethyl 3-methylcyclohexane-2-one-1-oxalate,  $CH_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CO} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , prepared by the action of ethyl oxalate and sodium on 1-methylcyclohexane-2-one in presence of light petroleum, loses carbon monoxide and yields ethyl 3-methylcyclohexane-2-one-1-carboxylate,



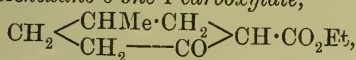
which boils at  $115^\circ$  under 12 mm. pressure and forms a semicarbazone,  $C_{11}H_{19}O_3N_3$ , melting at  $140^\circ$ . With isopropyl iodide and sodium ethoxide it forms ethyl 3-methyl-1-isopropylcyclohexane-2-one-1-carboxylate,  $C_6H_7OMePr^\beta \cdot CO_2Et$ , which boils at  $128^\circ$  under 10 mm. pressure, forms a semicarbazone only slowly, and on hydrolysis and elimination of carbon dioxide yields *m*-menthane-2-one,



this boils at 82° under 10 mm. pressure, has a sp. gr. 0·9128 at 15°, and reacts slowly with semicarbazide.

The following substances have been prepared in the same manner, starting from 1-methylcyclohexane-4-one.

*Ethyl 3-methylcyclohexane-6-one-1-carboxylate*,



boils at 110° under 10 mm. pressure and forms a *semicarbazone*,  $\text{C}_{11}\text{H}_{19}\text{O}_3\text{N}_3$ , melting at 134°.

*Ethyl 3-methyl-1-isopropylcyclohexane-6-one-1-carboxylate*,  $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \text{---CO} \end{array} \text{CPr}^\beta \cdot \text{CO}_2\text{Et}$ , boils at 125—127°

under 10 mm. pressure and forms a *semicarbazone*,  $\text{C}_{14}\text{H}_{25}\text{O}_3\text{N}_3$ , melting

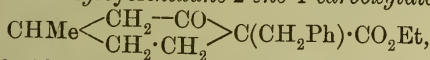
at 130°. *m-Menthane-4-one*,  $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \text{---CO} \end{array} \text{CHPr}^\beta$ , boils at 195°,

has a sp. gr. 0·8914 at 15°, and forms an *oxime*,  $\text{C}_{10}\text{H}_{19}\text{ON}$ , melting at 105°.

G. Y.

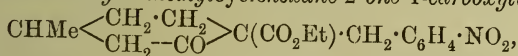
Syntheses by means of the Carboxylic Esters of Cyclic Ketones. III. Dicyclic Systems of indirectly connected Six-atom Rings. ARTHUR KÖTZ and GUSTAV KAYSER (*Annalen*, 1906, 348, 97—110. Compare Kötz and Hesse, this vol., i, 88; Kötz and Michels, preceding abstract).—The substances described in this paper were prepared by the action of the haloid compounds mentioned and sodium ethoxide on ethyl 4-methylcyclohexane-2-one-1-carboxylate in absolute alcoholic solution.

*Ethyl 1-benzyl-4-methylcyclohexane-2-one-1-carboxylate*,



from benzyl chloride, distils at 194° under 12 mm. pressure. The *semicarbazone*,  $\text{C}_{18}\text{H}_{25}\text{O}_3\text{N}_3$ , melts at 169°. When boiled with methyl-alcoholic potassium hydroxide, the ester yields 4-benzyl-1-methylcyclohexane-3-one,  $\text{C}_6\text{H}_8\text{OMe} \cdot \text{CH}_2\text{Ph}$ , which is colourless and boils at 166° under 10 mm. or at 173° under 13 mm. pressure; the *semicarbazone*,  $\text{C}_{15}\text{H}_{21}\text{ON}_3$ , melts at 172°; the *oxime*,  $\text{C}_{14}\text{H}_{19}\text{ON}$ , melts at 139°.

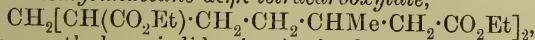
*Ethyl 1-p-nitrobenzyl-4-methylcyclohexane-2-one-1-carboxylate*,



from *p*-nitrobenzyl chloride, crystallises in glistening, golden-yellow needles and melts at 90·5°.

The action of phenacyl bromide on ethyl 4-methylcyclohexane-2-one-1-carboxylate and sodium ethoxide leads to the formation of bromodiphenacyl.

*Ethyl βκ-dimethylundecane-αεηλ-tetracarboxylate*,



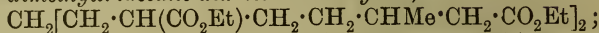
formed from methylene iodide, is obtained as a viscid oil boiling at 253° under 16 mm. pressure.

Only a small amount of ethyl β-methylpimelate is obtained from ethylene bromide, most of the ketone-ester being regained unchanged.

*Ethyl 4 : 4'-dimethyl-1 : 1'-trimethylenedicyclohexane-2 : 2'-dione-1 : 1'-dicarboxylate*,  $\text{C}_3\text{H}_6(\text{C}_6\text{H}_7\text{OMe} \cdot \text{CO}_2\text{Et})_2$ , formed from trimethylene dibromide, is obtained as a viscid oil which boils at 257—263° under

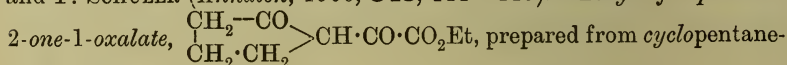


18 mm. pressure and is converted by the action of sodium ethoxide into *ethyl βμ-dimethyltridecane-αεν-tetracarboxylate*,

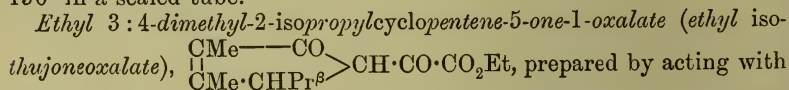


this forms a yellow oil boiling at 287—294° under 14 mm. pressure. When boiled with methyl-alcoholic potassium hydroxide, the dicarboxylate is hydrolysed, and decomposes, forming 1 : 1'-*dimethyl-4 : 4'-trimethylenedicyclohexane-3 : 3'-one*; this forms a *semicarbazone*,  $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_6$ , which melts at 107° and on treatment with sulphuric acid yields a small amount of a colourless oil boiling at about 204°. G. Y.

*αγ-Diketocarboxylic Esters of the cyclopentane and Bicyclo-(O : 1 : 3)-hexane Groups.* ARTHUR KÖTZ, ARTHUR BIEBER, and P. SCHÜLER (*Annalen*, 1906, 348, 111—119).—*Ethyl cyclopentane-2-one-1-oxalate*,



*Ethyl 3 : 4-dimethyl-2-isopropylcyclopentene-5-one-1-oxalate (ethyl isothujoneoxalate)*,



*Ethyl thujoneoxalate*,  $\text{CH}_2 \begin{array}{l} \text{CH} \text{---} \text{CHMe} \\ \text{CPr}^\beta \cdot \text{CH}(\text{CO} \cdot \text{CO}_2\text{Et}) \end{array} > \text{CO}$ , formed in similar manner to the *iso-ester*, boils at 168—170° under 11 mm. pressure; the *semicarbazone*,  $\text{C}_{15}\text{H}_{23}\text{O}_4\text{N}_3$ , melts at 156—157°. When boiled under the ordinary pressure for two days, the ester yields a mixture of thujone and *ethyl thujonecarboxylate*,  $\text{C}_{13}\text{H}_{20}\text{O}_3$ , which gives a violet coloration with ferric chloride. A similar mixture is obtained by heating the ethyl oxalate under pressure at 220°. On prolonged heating with dilute sulphuric acid, the ethyl oxalate yields oxalic acid, thujone, and *isothujone*, whilst with concentrated hydrochloric acid at 125° oxalic acid, carbon monoxide and dioxide, and *isothujone* are formed.

The behaviour, when heated under the ordinary pressure, of the product formed with sodium ethoxide and ethyl oxalate may be used to determine whether the group  $\text{---CH}_2 \cdot \text{CO}$  is present in a five- or six-atom ring.

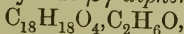
G. Y.

**Benzoylsalicylic** [*o*-Benzoyloxybenzoic] Acid. F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 169247).—*o*-Benzoyloxybenzoic acid,  $\text{OBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , and its salts have not hitherto been obtained, but the acid is prepared readily by treating disodium salicylate at low temperatures with 1 mol. or slight excess of benzoyl chloride diluted with petroleum or ether. The residue after pouring off the diluent is extracted with water and the *o*-benzoyloxybenzoic acid precipitated with acid and recrystallised from dilute alcohol. It is quite insoluble in cold water, dissolving sparingly on warming; it dissolves readily in ether, alcohol, or chloroform and does not give the reactions of salicylic acid until after hydrolysis with alkalis. The crystalline acid melts at  $132^\circ$ .

G. T. M.

**Reduction of  $\alpha\beta$ -Unsaturated Carboxylic Esters with Aluminium Amalgam.** FRANZ HENLE (*Annalen*, 1906, 348, 16—30. Compare Thiele and Buehner, this vol., i, 569; Harries and Eschenbach, *Abstr.*, 1896, i, 305; H. Wislicenus, *Abstr.*, 1896, i, 672).—Methyl cinnamate is reduced by aluminium amalgam and water in ethereal solution in four to six days, forming methyl dihydrocinnamate in a yield of 55—65 per cent., methyl  $\beta\gamma$ -diphenyladipate in a yield of 8—9 per cent., and an isomeride of the latter melting at  $73^\circ$  in a yield of 4—5 per cent.

*Methyl  $\beta\gamma$ -diphenyladipate*,  $\text{CO}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , crystallises from ethyl acetate, melts at  $175^\circ$ , is sparingly soluble in hot ether, alcohol, or light petroleum, but readily so in other hot organic solvents, does not decolorise potassium permanganate or bromine, and on hydrolysis yields  *$\beta\gamma$ -diphenyladipic acid*,

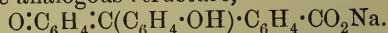


which crystallises from alcohol in small, glistening, colourless prisms, loses  $\text{C}_2\text{H}_6\text{O}$  at  $105^\circ$ , melts at about  $270^\circ$ , is insoluble in water, reddens moist litmus paper in alcoholic solution, and dissolves in aqueous sodium carbonate. When fused with potassium hydroxide, the acid is oxidised, forming benzoic and acetic acids.  *$\beta\gamma$ -Diphenyladipic diacetic anhydride*,  $\text{C}_4\text{H}_6\text{Ph}_2(\text{CO} \cdot \text{OAc})_2$ , formed by boiling the acid with acetyl chloride in a reflux apparatus, crystallises from light petroleum, melts at  $100$ — $105^\circ$ , resolidifies on further heating, and melts again to a yellow liquid at  $235$ — $240^\circ$ . It is soluble in chloroform, loses acetic anhydride slowly in a vacuum, quickly at  $140^\circ$ , forming a brown, granular mass, which is not the adipic anhydride, melts at  $225$ — $240^\circ$ , and is soluble in boiling nitrobenzene. The mixed anhydride is hydrolysed by boiling water, forming acetic and  *$\beta\gamma$ -diphenyladipic acids*. A white substance, only sparingly soluble in chloroform and insoluble in aqueous sodium carbonate, is formed together with the mixed anhydride by the action of freshly-distilled acetyl chloride on  *$\beta\gamma$ -diphenyladipic acid*.

The isomeride of methyl  *$\beta\gamma$ -diphenyladipate*,  $\text{C}_{20}\text{H}_{22}\text{O}_4$ , melting at  $73^\circ$ , crystallises from hot light petroleum, is readily soluble in other organic solvents, and behaves as a saturated ester towards potassium permanganate and bromine. The acid,  $\text{C}_{18}\text{H}_{18}\text{O}_4$ , crystallises from water, melts at  $169$ — $170^\circ$ , has an acid reaction in aqueous solution, and is probably a stereoisomeride of the  *$\beta\gamma$ -diphenyladipic acid* melting at  $270^\circ$ .

Ethyl benzylmalonate is obtained in a 60 per cent. yield by the reduction of ethyl benzylidenemalonate with aluminium amalgam and moist ether. Ethyl cinnamylidenemalonate also is reduced by aluminium amalgam and moist ether. G. Y.

**Constitution of the Phenolphthalein and Quinolpthalein Salts.** ARTHUR G. GREEN and PERCY E. KING (*Ber.*, 1906, 39, 2365—2371).—A reply to Meyer and Spengler's criticism (*Abstr.*, 1905, i, 440) of the views of Green and Perkin (*Trans.*, 1904, 85, 398). The following facts prove the existence of coloured quinonoid alkyl esters of the phthaleins, such as  $\text{O}:\text{C}_6\text{H}_4:\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , and hence support the contention that the coloured alkali salts of the phthaleins have the analogous structure,



The analogy between the phthaleins and the fluoresceins, assumed in the previous paper, is thus made complete; the apparent differences between the two series are in reality merely differences of stability.

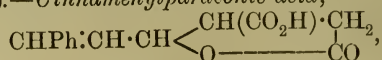
The ester,  $\text{O}:\text{C}_6\text{H}_4:\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , prepared by saturating a methyl-alcoholic solution of phenolphthalein containing zinc chloride with hydrogen chloride, and subsequently pouring the solution into ice-cold water, forms a scarlet-red precipitate, which is rapidly hydrolysed by water at the ordinary temperature, becoming colourless; even when dried in a desiccator, partial hydrolysis takes place, the colour changing from dark red to rose-red. The same red salt is apparently formed on heating phenolphthalein with methyl sulphate, giving a red solution, but it has not yet been isolated.

On passing hydrogen chloride through a solution of quinolphthalein in methyl alcohol, small, red crystals of the *chloride* of the *quinonoid methyl ester*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{smallmatrix}\text{O}\cdot\text{Cl}$ , separate; this substance is stable when dry and is much less easily decomposed by water than the quinonoid ester of phenolphthalein. When heated with aqueous alkalis it is, however, rapidly converted into the ordinary violet salts of quinolphthalein.

The *chloride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{smallmatrix}\text{O}\cdot\text{Cl}$ , of quinolphthalein, prepared by passing hydrogen chloride into a warm solution of the phthalein in glacial acetic acid, also forms red crystals; it is decomposed instantaneously by water, alcohol, or by ether containing alcohol.

W. A. D.

**Cinnamenylparaconic Acid.** J. BOUGAULT (*Compt. rend.*, 1906, 142, 1539—1541).—*Cinnamenylparaconic acid*,



prepared by the action of cinnamaldehyde on sodium succinate in the presence of acetic anhydride, melts at  $145^\circ$ , is very sparingly soluble in water, benzene, or light petroleum, sparingly soluble in ether or chloroform, a little more so in cold alcohol (0.5 to 0.6 per cent.), much more soluble in hot alcohol; it is reprecipitated immediately by a



strong acid from solution in sodium carbonate, but only after several hours from solution in sodium hydroxide; the *dibromide* is crystalline, and melts and decomposes at  $205^{\circ}$ ; it is very sparingly soluble in the ordinary solvents, dissolves readily in sodium carbonate, but when the solution is heated decomposition ensues with the formation of sodium bromide, benzaldehyde, and other products not yet examined.

Cinnamenylparaconic acid is readily converted by the action of boiling water into cinnamenylisocrotonic acid, which was the only product obtained by Fittig and Batt (Abstr., 1904, i, 744), who first examined the action of cinnamaldehyde on sodium succinate. M. A. W.

**Salts of Mineral Acids derived from the Phthaleins. I.** GUSTAV HELLER [and, in part, OTTO LANGKOPF] (*Zeit. Farb. Ind.*, 1906, 5, 265—269).—*Gallein hydrochloride alcoholate*,  $C_{20}H_{12}O_7 \cdot HCl \cdot C_2H_6O$ , prepared by di-solving gallein in alcoholic hydrochloric acid, crystallises in brown prisms or plates. The corresponding *acetone* derivative,  $C_{20}H_{12}O_7 \cdot HCl \cdot C_3H_6O$ , obtained from gallein, hydrochloric acid, and acetone, forms bluish-black needles. The formation of these substances can be utilised in purifying gallein. Pure gallein, obtained by decomposing either of the above compounds with concentrated sulphuric acid and adding water to the filtered solution, differs from ordinary gallein by giving only a slight yellowish-red coloration when dissolved in alcohol or acetone. *Gallein hydrochloride methyl alcoholate*,  $C_{20}H_{12}O_7 \cdot HCl \cdot MeOH$ , crystallises from methyl alcohol on adding ether in clusters of needles. *Gallein sulphate*,  $C_{20}H_{12}O_7 \cdot H_2SO_4$ , does not crystallise with alcohol or acetone. The *hydrobromide*, however, like the hydrochloride, crystallises from acetone with 1 mol. of the solvent.

Gallein ethyl ester gives with hydrochloric acid in presence of either alcohol or acetone the *hydrochloride*,  $C_{22}H_{16}O_7 \cdot HCl$ , which forms brownish-red needles and does not crystallise with the solvent. The analogous *sulphate*,  $C_{22}H_{16}O_7 \cdot H_2SO_4$ , is similar.

All the foregoing salts of gallein are decomposed by cold water. On adding an alcoholic solution of any one of them to boiling water, the reddish-brown *gallein hydrate*,  $C_{20}H_{12}O_7 \cdot H_2O$ , separates as a crystalline powder which loses  $1H_2O$  at  $180^{\circ}$ . A second modification of this substance, having a bluish-violet colour when dried in a vacuum, is obtained by adding the alcoholic solution of the salt to cold water, or by decomposing by a mineral acid the salts formed by gallein with alkalis. A third hydrated form is obtained as a blackish-red, crystalline powder on adding chloroform to a solution of pure gallein in acetone or by decomposing an alkali salt of gallein with acetic acid. Anhydrous gallein, obtained by expelling water from the hydrated forms or by fusing phthalic anhydride with pyrogallol, forms nearly black crystals. The relationship between the foregoing substances will be discussed in a subsequent paper. The alkali salts of gallein also exist in two modifications. The salt obtained by dissolving gallein in alkali is intensely violet; a red *potassium* salt,  $C_{20}H_{11}O_7K$ , is, however, formed on mixing alcoholic solutions of gallein and of potassium acetate.

Hydroxyquinolphthalein (Feuerstein and Dutoit, Abstr., 1901, i, 723) gives salts similar to those of gallein; the *hydrochloride ethyl*

*alcoholate*, *methyl alcoholate*, and *acetate* are described. The *sulphate*,  $C_{20}H_{12}O_7 \cdot H_2SO_4$ , does not crystallise with the solvent.

*Cærulein hydrochloride* and *sulphate* were prepared; these salts contain only about three-fourths of the amount of acid calculated for the formulæ  $C_{20}H_{10}O_6 \cdot HCl$  and  $C_{20}H_{10}O_6 \cdot H_2SO_4$  respectively. W. A. D.

**Compounds from Lichens. XV.** WILHELM ZOPF (*Annalen*, 1906, 346, 82—127. Compare Abstr., 1905, i, 212, 789).—The lichen, *Rhizoplaca chrysouleuca*, Zopf (*Lecanora chrysouleuca*, Ach; *Squamaria chrysouleuca*, or *Placodium chrysouleucum*), contains usnic acid and placodiolin, or, better, *placodiolic acid*,  $C_{17}H_{18}O_7$ , the latter of which dissolves when the plant is extracted with sodium hydrogen carbonate. It is precipitated from the solution with acid, and crystallises in leaflets or monoclinic, yellowish-green plates, melting at  $156—157^\circ$ ; in chloroform solution it has  $[\alpha]_D - 238^\circ$  at  $17^\circ$ ; its mol. weight was determined in acetone and cryoscopically in benzene, and found to be 315.6 in the one and 306 in the other solvent. In alkaline solution, the acid reduces potassium permanganate.

The usnic acid obtained from *Rhizoplaca opaca*, Zopf, has  $[\alpha]_D - 482.3^\circ$  at  $22^\circ$ , and was converted into Widman's decarbusnic acid melting at  $176^\circ$ .

Contrary to previous statements, neither zeorin nor sordidin was found in *Lecanora sulphurea*, but a crystalline substance melting at  $100^\circ$  was found together with usnic acid. It would appear that two modifications of this lichen exist, distinct in their chemical characters.

It is suggested that the rhizocarpinic acid melting at  $170^\circ$  described by Hesse is impure rhizocarpic acid which melts at  $177—179^\circ$ .

*Biatora Lightfootii* contains at least 6 per cent. of *l*-usnic acid ( $[\alpha]_D - 455.9^\circ$ ), to which is ascribed the yellowish- or greyish-green colour of the thallus. A colourless, crystalline compound is also present in small quantities.

The lichen, *Biatora granulosa* (*Lecidea granulosa* var. *decolorans*, *Patellaria decolorans*), contains gyrophoric acid melting at  $202—203^\circ$ , which, when heated with alcohol in a closed tube, yields ethyl orsellate melting at  $132^\circ$ . The presence of paretin is probably the cause of the violet colour which extracts of *Blastenia Jungermanniae* give with alkali hydroxides.

*Diploschistessic acid*,  $C_{15}H_{16}O_7$ , is present to the extent of 2—3 per cent., together with atranoric acid, in *Diploschistes scruposus* (*Patellaria scruposa* or *Urceolaria scruposa*); it crystallises in short needles or rosettes of leaflets melting at  $164—165^\circ$ ; its mol. weight was determined in acetone solution; it dissolves in alkali hydroxides to a yellow solution; its alcoholic solution is coloured violet by ferric chloride, and with bleaching powder it gives first a red, then a violet, and finally an indigo coloration. It is converted by acetic acid into orsellic acid, by alcohol into ethyl orsellate; it immediately reduces potassium permanganate, and is changed by potassium hydroxide into a substance resembling orcinol. From these characters it is concluded that this acid is a derivative of orsellic acid, but different from patellie acid and other orsellie acid derivatives. It is suggested that the acid described by Hesse as lecanoric acid in *Urceolaria bryophila* is impure

diploschistessic acid. *Cladina rangiferina* contains, together with atranoric acid, fumarprotocetraric acid and not cetraric acid. In *Cladina destrieta* the presence of destrietic acid cannot be affirmed, although a colourless compound is present together with *l*-usnic acid.

*Cladina silvatica* (*Cladonia rangiferina* var. *silvatica*) contains *d*-usnic acid ( $[\alpha]_D + 491.4^\circ$  in chloroform solution at  $22^\circ$ ), and thus differs from other Cladoniaceæ; the cetrarin also present is probably fumarprotocetraric acid.

The lichen, *Cladina silvatica* var. *spumosa* (*Cladonia rangiferina* var. *spumosa* or *Cladonia silvatica* var. *sylvestris*) cannot be regarded, as hitherto, simply as a variety of *Cladina silvatica*, since it contains 0.7 per cent. of *l*-usnic acid ( $[\alpha]_D - 490.8^\circ$  at  $17^\circ$  in chloroform solution). It is rather to be regarded as a variety of *Cladina alpestris*, and named *Cl. alpestris* var. *spumosa*.

Leiphæmin, which is found in *Hæmatomma leiphæmum*, forms rhombic crystals. In the lichen, *Hæmatomma porphyrium*,  $\frac{1}{2}$  per cent. of atranoric acid, 1 per cent. of zeorin, 1 per cent. of porphyrilic acid, 1 per cent. of leiphæmin, and a small amount of hymenorhodin are found. The last mentioned crystallises in rhombic, red plates and gives purple or violet colorations with alkalis and sulphuric acid; it would thus appear to be an anthracene derivative. These facts show that the view that *Hæmatomma porphyrium* and *H. leiphæmum* are identical is untenable. *Hæmatomma coccineum* (*Hæmatomma coccineum* var. *ochroleucum* or *Lecanora hæmatomma coccinea*) contains *l*-usnic acid  $2\frac{1}{2}$ , zeorin  $\frac{1}{2}$ , atranoric acid about  $\frac{1}{3}$ , porphyrilic acid 2, and leiphæmin 2 per cent., also a very small quantity of hymenorhodin; Hesse's hæmatommidin is probably identical with leiphæmin.

*Parmelia Mougeotti* contains *d*-usnic acid.

*Lepraria candelaris* contains 20—22 per cent. of calycin; the presence of pinastric acid was not established. *Cyphelium trichiale* var. *candelare* contains 8 per cent. of calycin.

K. J. P. O.

*o*-Nitrobenzophenone and its Reduction Products. CARLO BAEZNER and AUGUST GARDIOL (*Ber.*, 1906, 39, 2512—2514).—

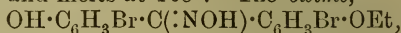
*Phenyldihydroanthranil*,  $C_6H_4 \begin{smallmatrix} \text{CHPh} \\ \text{NH} \end{smallmatrix} \text{O}$ , is prepared by reduction of *o*-nitrobenzophenone with aluminium amalgam in ethereal solution, or electrolytically in aqueous-alcoholic sodium acetate solution, with a lead cathode and a lead anode in cold saturated aqueous sodium carbonate; it forms glistening, pale yellow crystals and melts at  $116.5^\circ$ .

G. Y.

Observations in the Diphenylmethane and Xanthone Series. OTTO DIELS and KARL ROSENMUND (*Ber.*, 1906, 39, 2358—2364).—The substance formerly described as 5:5'-dibromo-2-hydroxy-2'-ethoxybenzophenone,  $CH \begin{smallmatrix} \text{CH} \cdot C(OH) \\ \text{CBr} = CH \end{smallmatrix} C \cdot CO \cdot C \begin{smallmatrix} C(OEt) \cdot CH \\ CH = CBr \end{smallmatrix} CH$  (*Abstr.*, 1905, i, 432), is shown by the following facts to have this structure, and not that of an alcoholate of 2:7-dibromoxanthone, as might be supposed from the ease with which it is converted into the latter substance. The reason for its instability is discussed at length.



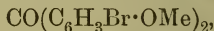
With phenylhydrazine, the substance gives the *phenylhydrazone*  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{C}(\text{:N}_2\text{HPh})\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{OEt}$ , which crystallises from alcohol in yellow needles and melts at  $165^\circ$ . The *oxime*,



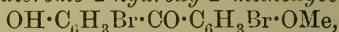
crystallises from chloroform and melts at  $181\text{--}182^\circ$ . The *acetyl* derivative,  $\text{OAc}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{OEt}$ , is easily obtained by direct acetylation, crystallises from alcohol in needles, and melts at  $105\text{--}107^\circ$ .

The monoethyl ether is easily reconverted into the diethyl ether  $\text{CO}(\text{C}_6\text{H}_3\text{Br}\cdot\text{OEt})_2$ , by treating it with potassium in benzene solution and heating the product with ethyl iodide. The ease, however, with which it is converted into 2:7-dibromoxanthone is shown by the fact that this substance begins to separate almost immediately on heating with  $N/20$  potassium hydroxide.

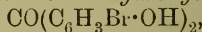
5:5'-Dibromo-2:2'-dimethoxydiphenylmethane,  $\text{CH}_2(\text{C}_6\text{H}_3\text{Br}\cdot\text{OMe})_2$ , prepared by adding 20 per cent. formaldehyde to a solution of *p*-bromoanisole in dilute sulphuric acid at  $-10^\circ$ , crystallises from alcohol and melts at  $108^\circ$ . On oxidation with chromic acid in glacial acetic acid solution, it gives 5:5'-dibromo-2:2'-dimethoxybenzophenone,



which crystallises from alcohol or glacial acetic acid and melts at  $123^\circ$ ; on heating this with concentrated hydrochloric acid for five hours at  $160^\circ$ , 5:5'-dibromo-2-hydroxy-2'-methoxybenzophenone,



is obtained. The latter crystallises from alcohol in deep yellow needles, melts at  $159^\circ$ , and differs from the analogous ethoxy-derivative in giving 5:5'-dibromo-2:2'-dihydroxybenzophenone,



when it is heated with aluminium chloride and the product decomposed by water; the dihydroxy-compound crystallises from light petroleum in yellow leaflets, melts at  $138.5^\circ$ , and differs from its monomethyl and monoethyl ethers by not being convertible into dibromoxanthone by concentrated acids or alkalis, or by phosphorus oxide or zinc chloride. With diazomethane, however, yellow needles melting at  $156^\circ$  are obtained, which, on heating with alkali, readily give the 2:7-dibromoxanthone.

W. A. D.

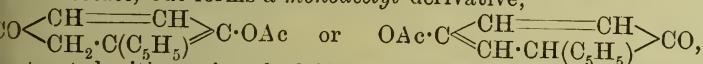
**Hydrobenzoin.** AUGUST KLAGES (*Ber.*, 1906, 39, 2356—2357).—The product obtained by treating benzoin according to Apitzsch and Metzger's method (*Abstr.*, 1904, i, 510) is not hydrobenzoin, but unchanged benzoin; its true nature is shown by the properties of its derivatives. Apitzsch and Metzger were probably led into error owing to the melting point of hydrobenzoin being identical with that of benzoin.

W. A. D.

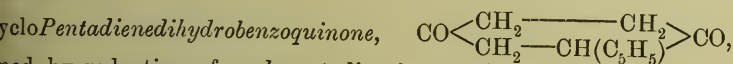
**Additive Products of cyclopentadiene and Quinones.** WALTHER ALBRECHT (*Annalen*, 1906, 348, 31—49).—With 1—2 mols. of cyclopentadiene, benzoquinone forms *additive* compounds, to which no satisfactory constitutions can be ascribed; those given are in accordance with most of the properties of the substances, but not with the reduction of cyclopentadienequinone to a dihydro-derivative which is

quinol, nor with the stability of the chloranil derivative of *cyclopentadiene*.

*cyclopentadienebenzoquinone*,  $\text{CH} \begin{smallmatrix} \text{CH} - \text{CO} \\ \text{CO} - \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{C}_5\text{H}_5$ , formed with development of heat by the action of 1 mol. of *cyclopentadiene* on 1 mol. of benzoquinone in cooled alcoholic solution, crystallises in long, slender, slightly yellow needles, or flat, greenish-yellow prisms, melts at 77—78°, decomposes into its generators when more highly heated, is readily soluble in organic solvents, and gives in alkaline solution a deep red to yellow, in concentrated sulphuric acid a red coloration, and a blue, flocculent precipitate on addition of water. It forms an intense blue solution when heated with zinc chloride and glacial acetic acid, reduces ammoniacal silver nitrate at the ordinary temperature and Fehling's solution on boiling, forms an unstable *dibromide*, and is precipitated with hydroxylamine and phenylhydrazine. When esterified with acetic anhydride, *cyclopentadienebenzoquinone* yields *acetyl diacetate*, but forms a *monoacetyl* derivative,



when treated with acetic anhydride and cooled concentrated sulphuric acid; this crystallises in white needles, melts at 91—92°, gives a blue coloration with glacial acetic and concentrated sulphuric acids, and yields benzoquinone when boiled with ferric chloride solution. The *semicarbazone* of *cyclopentadienebenzoquinone*,  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_6$  or  $\text{H}_{18}\text{O}_3\text{N}_6$ , forms a fine, white powder, decomposes at about 150°, and gives an intense yellow coloration with concentrated sulphuric acid.

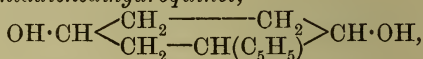


formed by reduction of *cyclopentadienebenzoquinone* by zinc dust in glacial acetic acid solution, separates from alcohol in white crystals, melts at 34—35°, decomposes when distilled, forming *cyclopentadienequinol*, is soluble in the usual solvents, gives a reddish-violet coloration with concentrated sulphuric acid, reduces ammoniacal silver nitrate and Fehling's solutions at the ordinary temperature, and is converted by concentrated potassium hydroxide into an insoluble, dark *polymeride*,  $(\text{C}_{11}\text{H}_{12}\text{O}_2)_x$ , melting above 270°. The dihydroketone forms a yellow *precipitate* with phenylhydrazine in aqueous solution, a *semicarbazone* melting at 222—224°, and with Baeyer's reagent a *ferrocyanide* crystallising in long, colourless needles. The *phenylhydrazone*,  $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2$ , crystallises in white needles and decomposes at 150°. With bromine in ethereal solution, the dihydrodiketone forms a *hydroxybromide*,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{Br} \cdot \text{OH}$ , which crystallises in colourless prisms, melts at 132—133°, absorbs 1 mol. of bromine in chloroform solution, and when boiled with a copper-zinc couple and acetic acid alcoholic solution yields the dihydrodiketone. The *dibromide*,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{Br}_2$ , is formed in slender needles by the action of hydrogen peroxide on the hydroxybromide in chloroform solution and melts at 139—139°. The action of methyl-alcoholic potassium hydroxide on the hydroxybromide leads to the formation of the *oxide*,  $\text{C}_{11}\text{H}_{12}\text{O}_3$ , which crystallises in small prisms, melts at 149—150°, and re-forms

the hydroxybromide when treated with hydrogen bromide in glacial acetic acid solution.

The *pinacone*,  $C_{22}H_{22}O_4$ , formed together with the dihydrodiketone by the reduction of *cyclopentadienebenzoquinone* with zinc dust, crystallises in white leaflets, melts at  $188-189^\circ$ , gives a reddish-violet coloration with concentrated sulphuric acid, reduces ammoniacal silver nitrate on boiling, or dilute potassium permanganate at the ordinary temperature, and forms a deep red, sparingly soluble product with phenylhydrazine.

*trans-cyclopentadienedihydroquinol*,



prepared together with a yellow oil,  $C_{11}H_{16}O_2, \frac{1}{2}H_2O$ , which is probably the *cis-form*, by reduction of dihydro*cyclopentadienebenzoquinone* with sodium amalgam, crystallises in stellate aggregates of needles, melts at  $88^\circ$ , and on exposure to air absorbs  $\frac{1}{2}H_2O$ , forming dull crystals melting at  $96-98^\circ$ . The *dibenzoate*,  $C_{25}H_{24}O_4$ , crystallises in slender needles and melts at  $166-167^\circ$ .

With chloranil, *cyclopentadiene* reacts in benzene solution in presence of trimethylamine, forming the *additive* compound,  $C_{11}H_6O_2Cl_4$ , which crystallises from absolute alcohol in long, strongly refracting yellow needles, melts at  $146-146.5^\circ$ , gives with concentrated sulphuric acid a violet, with alcoholic potassium hydroxide a yellowish-red solution, reduces ammoniacal silver nitrate on boiling, reacts violently with phenylhydrazine, and with bromine in chloroform solution under direct sunlight forms a *dibromide*,  $C_{11}H_6O_2Cl_4Br_2$ , crystallising in glistening, white leaflets and melting at  $269^\circ$ .

*cyclopentadiene- $\alpha$ -naphthaquinone*,  $C_{15}H_{12}O_2$ , prepared from *cyclopentadiene* and  *$\alpha$ -naphthaquinone* in benzene solution, crystallises in slender, white prisms, melts at  $115-116^\circ$ , reduces ammoniacal silver and Fehling's solutions at the ordinary temperature, gives a red coloration with alkali hydroxides or concentrated sulphuric acid, and forms *precipitates* with phenylhydrazine and semicarbazide acetates.

*Dicyclopentadienebenzoquinone*,  $CO < \begin{array}{c} CH_2 \cdot CH(C_5H_5) \\ CH(C_5H_5) \cdot CH_2 \end{array} > CO$ , formed by the action of 2 mols. of *cyclopentadiene* on 1 mol. of *benzoquinone* in benzene or alcoholic solution, crystallises in glistening, white leaflets or needles, melts at  $157-158^\circ$ , is soluble in organic solvents, only slightly volatile in a current of steam, is insoluble in aqueous alkali hydroxides, reduces ammoniacal silver and Fehling's solution on boiling, behaves in the same manner as *cyclopentadienebenzoquinone* towards concentrated sulphuric acid and zinc and ferrous chlorides, and forms a red oil with phenylhydrazine and an insoluble white *disemicarbazone*, melting above  $270^\circ$ . The *dioxime*,  $C_{16}H_{18}O_2N_2$ , crystallises from alcohol, becomes brown at  $185^\circ$ , and does not melt at  $270^\circ$ . With bromine in chloroform solution, *dicyclopentadienebenzoquinone* forms a *dibromide* which, on recrystallisation from alcohol yields the *ethoxybromide*,  $C_{18}H_{21}O_3Br$ , crystallising in slender, white needles and melting at  $142^\circ$ . The *methoxybromide*,  $C_{17}H_{19}O_3Br$ , crystallises in slender, white needles and melts at  $188^\circ$ .

*cyclopentadiene* does not react with anthraquinone, phenanthrene



quinone,  $\beta$ -naphthaquinone, benzil, benzylideneacetone, phorone, or dibenzoylstyrene. G. Y.

**Anthraquinone- $\alpha$ -sulphonic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 167169).— $\alpha$ -Nitroalizarin and  $\alpha$ -nitroanthraquinonesulphonic acids behave like  $\alpha$ -nitroanthraquinone on treatment with hot aqueous alkali sulphites, the  $\alpha$ -nitro-group being replaced by a sulpho-group.

$\alpha$ -Nitroalizarin and  $\alpha$ -nitroanthraquinone-6-sulphonic acid, when treated in this way, give rise to alizarin- $\alpha$ -sulphonic and anthraquinone-1:6-disulphonic acids respectively. The  $\alpha$ -nitroanthraquinonesulphonic acids, containing their sulphonic groups in positions 5, 7, and 8, behave in a similar manner. G. T. M.

**Preparation of Anthraquinone-di- and -tri-sulphonic Acids.** R. WEDEKIND & Co. (D.R.-P. 170329).—Potassium anthraquinone- $\alpha$ -sulphonate, when sulphonated with fuming sulphuric acid in the presence of mercury, yields anthraquinone-1:5- and -1:8-disulphonic acids. In the absence of mercury, the sulphonation leads to the production of the 1:7- and 1:6-disulphonic acids and a trisulphonic acid of unknown constitution. On heating this mixture of acids under pressure with milk of lime containing calcium chloride and potassium nitrate, 1:7- and 1:6-dihydroxyanthraquinones are produced, together with about 25 per cent. of a new *dihydroxyanthraquinonesulphonic acid*, the barium salt,  $C_{28}H_{14}O_{14}S_2Ba$ , of which crystallises from hot water in orange needles. G. T. M.

**Preparation of the Carbamates of the Nitroaminoanthraquinones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 67410).—*o*-Nitro-derivatives of the aminoanthraquinones cannot be prepared either from the aminoanthraquinones themselves or from their cycl derivatives. In the former case, the nitration does not proceed smoothly, and in the latter only *p*-nitro-derivatives are produced. Nitration of the carbamates of the aminoanthraquinones, however, leads to the production of the important *o*-nitroamino-derivatives. The carbamate of  $\beta$ -aminoanthraquinone, obtained by heating together  $\beta$ -aminoanthraquinone and ethyl chlorocarbonate in nitrobenzene solution, separates on cooling in golden-yellow leaflets; on nitration with a mixture of concentrated nitric and sulphuric acids, it yields 1-nitro-2-aminoanthraquinone and 3-nitro-2-aminoanthraquinone, these isomerides being separated by crystallisation from nitrobenzene, in which the latter is the less soluble. Similarly, the carbamate of  $\alpha$ -aminoanthraquinone furnishes a mixture of the ortho- and para-nitro-compounds, which are also separated by means of nitrobenzene, in which the para-isomeride is the less soluble. G. T. M.

**Preparation of  $\alpha$ -Nitro- $\beta$ -methoxyanthraquinones.** FARBERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 167699).—The energetic nitration of anthraquinone in concentrated sulphuric acid solution gives rise to the 1:5- and 1:8-dinitroanthraquinones as chief products, but 40 per cent. of the nitrated material consists of a

mixture of other isomerides which have been separated by fractional crystallisation from nitrobenzene and other solvents and characterised by conversion into dimethoxyanthraquinones and dihydroxyanthraquinones successively.

The  $\beta\beta$ -dinitroanthraquinones are present only in very small quantities in the product of nitration. The  $\alpha\beta$ -isomerides, of which the 1:6-compound is formed in largest amount, behave differently from the  $\alpha\alpha$ -compounds towards sodium methoxide. In the  $\alpha\beta$ -series, the  $\beta$ -nitro-group is readily replaced by methoxyl, and an  $\alpha$ -nitro-methoxyanthraquinone results; the  $\alpha\alpha$ -compounds are attacked only with great difficulty, and then both nitro-groups are replaced by methoxyl.

1-Nitro-6-methoxyanthraquinone is readily formed by heating together 1:6-dinitroanthraquinone and sodium methoxide in methyl alcohol; it crystallises from benzene in lustrous, yellow leaflets melting at 26°. With concentrated sulphuric acid, the methoxy-derivative develops a bright orange colour; it dissolves in aqueous sodium sulphide to a pale bluish-green solution, from which, on warming, 1-amino-6-methoxyanthraquinone separates as an orange-yellow precipitate.

1-Nitro-7-methoxyanthraquinone crystallises from benzene in slightly coloured needles melting at 238°; on reduction with sodium sulphide, it furnishes the orange-red 1-amino-7-methoxyanthraquinone.

These methoxy-derivatives are readily hydrolysed to  $\alpha$ -nitrohydroxyanthraquinones by concentrated hydrochloric and acetic acids. The  $\alpha$ -amino- $\beta$ -hydroxyanthraquinones may be obtained either by reducing the  $\alpha$ -nitro- $\beta$ -hydroxy-derivatives or by hydrolysing the  $\alpha$ -amino- $\beta$ -methoxy-derivatives.

The patent contains a table of the properties of the dinitro- and dimethoxy-anthraquinones.

G. T. M.

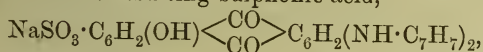
**A New Derivative of Anthraquinone.** FARBENFABRIK VORM. FRIEDR. BAYER & Co. (D.R.-P. 167461).—Although the fusion of erythrohydroxyanthraquinone with potassium hydroxide furnishes a certain amount of alizarin, yet the main product of this reaction is a substance,  $C_{28}H_{14}O_6$ , hitherto uncharacterised, which, in view of its sparing solubility, is probably formed by the condensation of 2 molecules of erythrohydroxyanthraquinone; the alkali salts of this compound, which are also very insoluble, point to its being a hydroxy-derivative. It crystallises from diphenylmethylamine in golden-yellow needles, and yields with alkaline solutions of sodium hyposulphite a leuco-derivative which is somewhat more soluble in aqueous alkali.

G. T. M.

**Preparation of *p*-Mono- and *p*-Di-chloroanthrarufin.** WEDEKIND & Co. (D.R.-P. 167743).—Hitherto anthrarufin has only been successfully chlorinated when suspended or dissolved in glacial acetic acid. It is now found that when suspended in dilute sulphuric acid boiling at 140° and treated slowly with the calculated amount of potassium chlorate and sodium chloride in aqueous solution, anthrarufin may be quantitatively converted into either *p*-mono- or *p*-chloroanthrarufin.

G. T. M.

[Sulphonation of  $\alpha$ -Hydroxyquinizarin-green.] FARBEN-  
 BRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 170113).— $\alpha$ -Hydroxy-  
 quinizarin-green,  $\text{HO} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{NH} \cdot \text{C}_7\text{H}_7)_2$ , when sulphonated  
 the usual way, yields mono- and di-sulphonic derivatives containing  
 the sulpho-groups in the toluene nuclei. When, however, the sul-  
 onation is effected by fuming sulphuric acid in the presence of boric  
 acid, the sulpho-groups enter the anthraquinone residue exclusively.  
 The sodium salt of the resulting sulphonic acid,



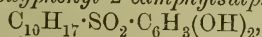
sparingly soluble in hot water, but dissolves more readily in dilute  
 acetic acid. Its colour in concentrated sulphuric acid is violet-blue,  
 whereas the other sulphonic acids of  $\alpha$ -hydroxyquinizarin-green  
 develop greenish-blue or bluish-green colorations. G. T. M.

Thioborneol and other Derivatives of Camphane con-  
 taining Sulphur. WALTHER BORSCHKE and W. LANGE (*Ber.*, 1906,

2346—2356).—*Camphane-2-sulphinic acid*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{SO}_2\text{H} \\ | \\ \text{CMe}_2 \\ | \\ \text{CH}_2 \cdot \text{CH} - \text{CH}_2 \end{array}$ ,

prepared by saturating an ice-cold ethereal solution of magnesium  
 phenyl chloride with sulphur dioxide, forms a colourless syrup, which  
 is only sparingly soluble in water; when cooled in a mixture of ice  
 and salt, it gelatinises, but does not crystallise. The *sodium* salt,  
 $\text{C}_{10}\text{H}_{17} \cdot \text{SO}_2\text{Na}$ , crystallises from water.

*Methylcamphylsulphone*,  $\text{C}_{10}\text{H}_{17} \cdot \text{SO}_2\text{Me}$ , prepared by warming the  
 sulphinic acid with alcoholic sodium ethoxide and methyl iodide,  
 crystallises from dilute alcohol in long, slender needles and melts at  
 $-58^\circ$ . 1:4-*Dihydroxyphenyl-2-camphylsulphone*,



prepared by the action of the sulphinic acid on benzoquinone, separates  
 from benzene or glacial acetic acid in colourless crystals and melts at  
 $5-187^\circ$ .

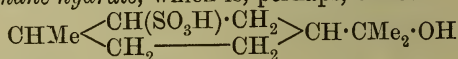
*Camphane-2-sulphonic bromide*,  $\text{C}_{10}\text{H}_{17} \cdot \text{SO}_2\text{Br}$ , prepared by the action  
 of bromine at  $0^\circ$  on camphylsulphinic acid dissolved in aqueous  
 potassium hydroxide, forms a nearly colourless oil, which, with  
 ammonia, gives *camphane-2-sulphonamide*; this crystallises from a  
 mixture of benzene and light petroleum and melts at  $122-123^\circ$ .

*Thioborneol (camphyl hydrosulphide)*,  $\text{C}_{10}\text{H}_{17} \cdot \text{SH}$ , prepared either by  
 reducing camphane-2-sulphonic bromide with tin and hydrochloric acid  
 or by adding powdered sulphur to an ethereal solution of magnesium  
 phenyl chloride, boils at  $205-215^\circ$  and separates from dilute alcohol  
 as a white, crystalline mass which soon becomes caked to a glassy  
 duct; it softens gradually when heated, without melting at any  
 definite temperature; at  $50^\circ$ , it is completely liquid. By air it is  
 oxidised to *camphyl disulphide*,  $(\text{C}_{10}\text{H}_{17})_2\text{S}_2$ , which separates from dilute  
 alcohol in flocculent masses of crystals and melts (when not fully  
 purified) at  $121^\circ$ . The *mercuric chloride* derivative,  $\text{C}_{10}\text{H}_{17} \cdot \text{S} \cdot \text{HgCl}$ ,  
 thioborneol is a white powder; the *lead* derivative,  $(\text{C}_{10}\text{H}_{17}\text{S})_2\text{Pb}$ ,  
 is lustrous, yellow crystals.

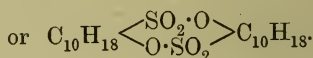
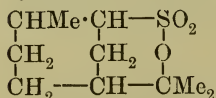


*Methyl camphyl sulphide* (thioborneol methyl ether),  $C_{10}H_{17} \cdot SMe$ , is best prepared by warming methyl iodide with an ethereal solution of the crude product of the action of sulphur on magnesium camphyl chloride; it forms a yellow oil, which boils at  $110-115^\circ$ , and combines with methyl iodide, giving *dimethylcamphylsulphonium iodide*,  $C_{12}H_{23}SI$ ; this crystallises from water, undergoing but slight decomposition in the process, in colourless plates, melts at  $148-148.5^\circ$ , and is converted by moist silver oxide into *dimethylcamphylsulphonium hydroxide*. The latter forms hygroscopic leaflets, melts at  $140-141^\circ$  and gives a crystalline *platinichloride*,  $(C_{12}H_{23}S)_2PtCl_6$ , which melts at  $142-143^\circ$ .

Camphane-2-sulphinic acid, on oxidation with potassium permanganate, gives not the corresponding sulphonic acid, but the *sulphonic acid* of a *camphane hydrate*, which is, perhaps, either



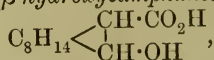
or  $OH \cdot CMe \begin{array}{c} \text{CH}(SO_3H) \cdot CH_2 \\ \text{CH}_2 \text{---} CH_2 \end{array} CHMe_2$ . The same substance is obtained on hydrolysing camphane-2-sulphonic bromide with 10 per cent. aqueous potassium hydroxide. The *potassium salt*,  $C_{10}H_{19}O_4SK$  crystallises from absolute alcohol and gives, with phosphorus pentachloride, *camphane hydrate sulphonic chloride*,  $C_{10}H_{19} \cdot SO_2Cl$ , which form colourless crystals and melts at about  $95^\circ$ . On reducing this sulphonichloride with tin and hydrochloric acid, a *product* having the composition  $C_{10}H_{18}O_3S$  is obtained, which separates from methyl or ethyl alcohol in colourless crystals and is reconverted into potassium camphane hydrate sulphonate by heating with dilute aqueous potassium hydroxide. The substance  $C_{10}H_{18}O_3S$  is perhaps the *auto-ester*.



W. A. D.

**Constitution of Camphor and its Derivatives. IX. Electrolytic Reduction of Camphorcarboxylic Acid to Borneolcarboxylic Acid and Dehydroborneolcarboxylic Acid.** JULIUS BREDT [and KARL BURKHEISER] (*Annalen*, 1906, 348, 199-209).—When reduced electrolytically in potassium carbonate solution with cathode of potassium amalgam, an *E.M.F.* of 30 volts, and a current of 7-7.5 amperes, the temperature remaining below  $30^\circ$ , camphorcarboxylic acid yields borneolcarboxylic acid and an *isomeride* which crystallises in needles and melts at  $101-102^\circ$ .

*Borneolcarboxylic acid* ( $\beta$ -hydroxycamphanecarboxylic acid),



crystallises from boiling water in silky needles, melts at  $170-171^\circ$  and when quickly heated distils at  $190^\circ$  under 13 mm. pressure. The *calcium salt*,  $(C_{11}H_{17}O_3)_2Ca$ , was analysed. When repeatedly distilled slowly under 13 mm. pressure into a sealed receiver, the acid loses water and yields *dehydroborneolcarboxylic acid* (*camphenecarboxylic acid*),  $C_{11}H_{16}O_2$ , which crystallises in fan-like aggregates of long

needles, melts at 112—113°, is volatile in a current of steam, and decolorises potassium permanganate, being oxidised to a crystalline acid melting at 209—210°.

Borneolcarboxylic acid is probably related to *trans*-camphylglycol (Farbwerke vorm. Meister, Lucius, & Brüning, Abstr., 1902, i, 299) as a hydroxy-acid to its glycol, dehydroborneolcarboxylic acid corresponding with dehydrocamphylcarbinol.

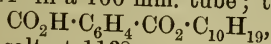
G. Y.

**Carvone.** HANS RUPE (*Ber.*, 1906, 39, 2372. Compare Rupe and Dorschky, this vol., i, 595).—Carvone semicarbazone, melting at 162°, has  $[\alpha]_D + 115.1^\circ$  at 20°; the semicarbazone melting at 141—142° has  $[\alpha]_D + 113.3^\circ$  at 20°.

W. A. D.

**Action of Sodamide on Cyclic Ketones. Derivatives of Fenchone and of Camphenilone, and their Constitution.** FRIEDRICH W. SEMMLER (*Ber.*, 1906, 39, 2577—2582).—*Dihydrofencholenamide* (b),  $C_{10}H_{19}ON$ , is obtained in quantitative yield when sodamide (1 mol.) and fenchone (1 mol.) react for four hours in boiling benzene; it melts at 94°, boils at 160° under 11 mm. pressure, and with concentrated sulphuric acid and potassium nitrite gives a brown coloration changing through red to green. A 25 per cent. ethereal solution has  $\alpha_D$  about  $+1^\circ$  in a 100 mm. tube. The substance is different from Mahla's amide (Abstr., 1902, i, 106), which is subsequently called dihydrofencholenamide (a).

By hydrolysis with alcoholic potash, *dihydrofencholenic acid* (b),  $C_{10}H_{18}O_2$ , is obtained; it solidifies at the ordinary temperature, boils at 140—141° under 10 mm. pressure, has a sp. gr. 0.9742 at 15°,  $n_D$  1.45862, and  $\alpha_D + 3.12^\circ$  in a 100 mm. tube. The *methyl* ester,  $C_{11}H_{20}O_2$ , boils at 91° under 12 mm. pressure, has a sp. gr. 0.9295 at 22°,  $n_D$  1.44260, and  $\alpha_D + 3.0^\circ$  in a 100 mm. tube. The *ethyl* ester boils at 97° under 10 mm. pressure, has a sp. gr. 0.9129 at 20°,  $n_D$  1.43958, and  $\alpha_D + 3.5^\circ$  in a 100 mm. tube. Dihydrofencholenic acid (a) boils at 140.5—141° under 10 mm. pressure, has a sp. gr. 0.9742 at 20°,  $n_D$  1.45962, and  $\alpha_D + 4.10^\circ$  in a 100 mm. tube (compare Mahla, *loc. cit.*); the *methyl* ester boils at 90° under 9 mm. pressure, has a sp. gr. 0.93306 at 22°,  $n_D$  1.44662, and  $\alpha_D + 3^\circ$  in a 100 mm. tube. *Dihydrofencholenyl alcohol* (b),  $C_{10}H_{20}O$ , obtained in an 80 per cent. yield by reducing the ethyl ester of the acid with sodium and alcohol, boils at 100° under 11 mm. pressure, has a sp. gr. 0.8869 at 22°,  $n_D$  1.45662, and  $\alpha_D + 10^\circ$  in a 100 mm. tube; the *acetate*,  $C_{10}H_{19}OAc$ , boils at 112—113° under 14 mm. pressure, has a sp. gr. 0.9123 at 22°,  $n_D$  1.44159, and  $\alpha_D + 12.44^\circ$  in a 100 mm. tube; the *phthalate*,



melts at 86°, the *silver* salt at 113°.

The corresponding (a) alcohol boils at 99—100° under 10 mm. pressure, has a sp. gr. 0.9072 at 22°, and  $n_D$  1.45762. *Dihydrofencholenaldehyde* (b),  $C_{10}H_{18}O$ , boils at 80—85° under 10 mm. pressure, has a sp. gr. 0.885 at 20°, and  $n_D$  1.445; the *semicarbazone* melts at 144—145°.

When camphenilone is treated with sodamide in benzene solution, *dihydrocamphoceanamide* (b),  $C_9H_{17}ON$ , is obtained; it melts at  $168^\circ$ , and by hydrolysis with alcoholic potash yields the *acid* (b),  $C_9H_{16}O_2$ , which boils at  $138-139^\circ$  under 12 mm. pressure, has a sp. gr. 0.9815 at  $22^\circ$ , and  $n_D$  1.45662. C. S.

**Synthesis of  $\Delta^{8(9)}$ -Menthene and of Active  $\Delta^{3,8(9)}$ -Menthadiene**  
FRIEDRICH W. SEMMLER and CH. RIMPEL (*Ber.*, 1906, 39, 2582—2587).—*isoPulegyl chloride*,  $C_{10}H_{17}Cl$ , is obtained quantitatively when *isopulegole* (1 mol) dissolved in light petroleum is slowly added to phosphorus pentachloride (1 mol.) in the same solvent, rise of temperature being avoided; it boils at  $85-90^\circ$  under 12 mm pressure, has a sp. gr. 0.9600 at  $20^\circ$ ,  $n_D$  1.47740,  $n_D + 19.15^\circ$  (100 mm tube), and by treatment with alcoholic potash yields *isopulegyl ether*,  $C_{10}H_{17}OEt$ , which boils at  $85-88^\circ$  under 14 mm. pressure and has a sp. gr. 0.8972 at  $20^\circ$ .

$\Delta^{8(9)}$ -*Menthene*,  $C_{10}H_{18}$ , is obtained when *isopulegyl chloride* is treated with sodium and boiling alcohol. It boils at  $53-55^\circ$  under 14 mm. pressure, has a sp. gr. 0.8104 at  $20^\circ$ ,  $n_D$  1.45662, and is optically inactive. By oxidation with dilute permanganate, it yields *p-menthane-8:9-diol*,  $C_{10}H_{18}(OH)_2$ , which boils at  $165^\circ$  under 26 mm pressure, and is oxidised by chromic acid to *p-methylhexahydroacetophenone*,  $C_9H_{16}O$ , which boils at  $70-73^\circ$  under 13 mm. pressure, has sp. gr. 0.8982 at  $20^\circ$ ,  $n_D$  1.44561, is optically inactive, forms a *semicarbazone*,  $C_{10}H_{19}ON_3$ , melting at  $164-165^\circ$ , and is oxidised by bromine in alkaline solution to *p-hexahydrotriluic acid*,  $C_8H_{14}O_2$ , which melts at  $108^\circ$ .

$\Delta^{3,8(9)}$ -*Menthadiene*,  $C_{10}H_{16}$ , is the chief product obtained when *isopulegyl chloride* dissolved in quinoline is added to quinoline at  $200-210^\circ$ ; it boils at  $62-65^\circ$  under 14 mm., or at  $174-177^\circ$  under the ordinary pressure, has a sp. gr. 0.8420 at  $20^\circ$ ,  $n_D$  1.48422, and  $n_D + 15^\circ$  (100 mm. tube). The presence of a conjugated system of two double linkings is proved by the fact that the hydrocarbon absorbs only two atoms of bromine.

The physical properties of Perkin's compounds (*Trans.*, 1905, 8, 639; 1906, 89, 839) do not agree with the preceding data; the discrepancy is attributed to intramolecular change, which occurs in the synthesis of Perkin's  $\Delta^{8(9)}$ -menthene and  $\Delta^{3,8(9)}$ -menthadiene. C. S.

**Synthesis of Menthene.** OTTO WALLACH (*Ber.*, 1906, 39, 2504—2505. Compare Semmler, preceding abstract; Perkin, *Trans.* 1906, 89, 837).—*Ethyl 1-hydroxy-4-methylcyclohexane-1-isobutyrate*,  $CHMe \begin{smallmatrix} <CH_2 \cdot CH_2> \\ <CH_2 \cdot CH_2> \end{smallmatrix} C \cdot (OH) \cdot CMe_2 \cdot CO_2Et$ , formed by condensation of 1-methylcyclohexane-4-one with ethyl  $\alpha$ -bromoisobutyrate in presence of zinc, boils at  $148-150^\circ$  under 16 mm. pressure, and on elimination of water yields *ethyl 4-methyl- $\Delta^1$ -cyclohexene-1-isobutyrate*,





which boils at 123—126° under 13 mm. pressure. The crystalline acid,  $\text{C}_{11}\text{H}_{18}\text{O}_2$ , obtained on hydrolysis of the unsaturated ester, melts at 95—96°, and when distilled slowly loses carbon dioxide and forms *i*- $\Delta^{4(8)}$ -menthene,  $\text{CHMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C} \cdot \text{CMe}_2$ . This boils at 172—174°, has a sp. gr. 0.831 and  $n_D$  1.4647 at 21°, and when oxidised with permanganate yields 1-methylcyclohexane-4-one and acetone. The action of amyl nitrite and hydrochloric acid, or successively of hydrochloric and nitrous acids, on *i*- $\Delta^{4(8)}$ -menthene leads to the formation of an additive compound, which is obtained as a blue oil, gradually solidifying to white crystals melting at 101—103°. Both forms of the substance are volatile in a current of steam and yield a menthylamine when reduced. When boiled with dilute sulphuric acid, *i*- $\Delta^{4(8)}$ -menthene is converted slowly into *i*- $\Delta^3$ -menthene.

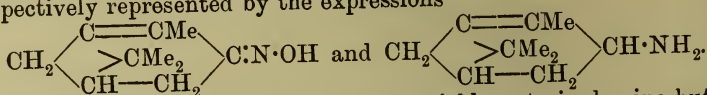
G. Y.

### Terpenes and Ethereal Oils. LXXVIII. Pinene Series.

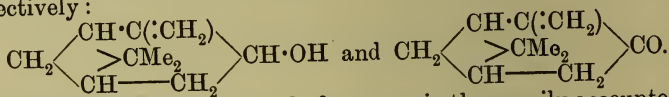
OTTO WALLACH (*Annalen*, 1906, 346, 220—247. Compare Abstr., 1894, i, 45; 1898, i, 485; this vol., i, 370).—The nitrosopinene obtained by the action of alkalis on pinene nitrosochloride is the oxime of an unknown ketone. Attempts have now been made to ascertain which is the ketone corresponding with this oxime, and secondly to determine the chemical relations of pinocarvone, which is obtained from nitrosopinene by conversion into pinylamine and thence into a ketone.

[With FRIEDRICH JÄGER.]—Pinocarveol is prepared by treating a solution of pinylamine with acetic acid and sodium nitrite, warming, and distilling the alcohol in steam; it has still to be separated from small quantities of nitrite and unchanged pinylamine; it is a colourless oil, boiling at 100—102° under 12 mm. pressure, and has a sp. gr. 0.980 and  $n_D$  1.4988 at 18°. The value of the molecular refraction shows that under this treatment the ring in pinylamine is not broken. With phenylcarbimide, pinocarveol yields mainly a well-crystallised product, melting at 82—84°, together with a small amount of a compound melting at 95°. When heated with a hydrogen sulphate or with sulphuric acid or with a solution of sulphuric acid in acetic acid, cymene is obtained in small quantity from pinocarveol. On oxidation with dilute permanganate, small amounts of a glycol and an acid,  $\text{C}_9\text{H}_{14}\text{O}_4$ , are formed. Pinocarvone is prepared from the alcohol in the manner previously described (Abstr., 1894, i, 45), and purified by conversion into the semicarbazone, which melts at 204°. The ketone boils at 95° under 12 mm. pressure, has a sp. gr. 0.984, and  $n_D$  1.5050 at 20°; from the value of the molecular refraction it is concluded that pinocarvone is the enolic form of a ketone with one ethylene linking. Pinocarvoneoxime (m. p. 98°) yields on reduction with sodium and alcohol a base isomeric with but different from pinylamine; it boils at 37—88° under 12 mm. pressure, and gives a carbamide which crystallises in needles melting at 99—100°. When oxidised with potassium permanganate, oxalic acid and a dibasic acid,  $\text{C}_9\text{H}_{14}\text{O}_4$ , are produced;

the latter melts at 96—97° and boils at 170—180° under 12 mm pressure. This acid is also formed by oxidation of pinocarveol, and appears to be identical with pinic acid. On this assumption, and using Wagner's formula for pinene, nitrosopinene and pinylamine are respectively represented by the expressions



Since the reduction of pinocarvoxime yields not pinylamine but an isomeride, it follows that in the replacement of the amino-group by hydroxyl a change in the linking must have taken place. Hence the following formulæ are suggested for pinocarveol and pinocarvone respectively:



The formation of pinic acid and of cymene is then easily accounted for but it is not obvious why the piceane ring of pinocarvone does not open with formation of carvone.

An optically active pinocarveol is contained in the less volatile fraction of the oil of *Eucalyptus globulus*, and is isolated by conversion into the hydrogen phthalate; it boils at 92° under 12 mm. pressure, has sp. gr. 0.9745 and  $n_D$  1.49630 at 20°, and  $[\alpha]_D -52.45^\circ$  in 12.75 per cent. ethereal solution. With phenylcarbimide it yields the same mixture of two compounds as does the artificial product. When oxidised with chromic acid in acetic acid solution, it is converted into a ketone,  $\text{C}_{10}\text{H}_{14}\text{O}$ , which yields with semicarbazide two semicarbazones, a soluble substance melting at 209—210°, and an insoluble, which crystallises in needles melting and decomposing at 320°. The oxime is crystalline and boils at 140° under 20 mm. pressure.

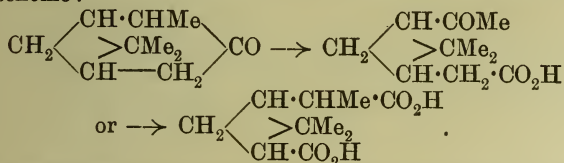
[With CURT ENGELBRECHT.]—Carvopinone is the ketone corresponding with nitrosopinene, and is obtained when the latter is digested with oxalic instead of mineral acids. It boils at 94—96° under 12 mm. pressure, and yields a characteristic semicarbazone, which crystallises in prisms unchanged at 300°. The ketone cannot be re-formed from the semicarbazone in a pure state. With hydroxylamine, nitrosopinene is re-formed. When reduced with sodium and alcohol, an alcohol is produced which on oxidation with chromic acid is converted into pinocamphone.

If a solution of nitrosopinene in acetic acid is boiled with oxalic acid or with 1 mol. of hydrochloric acid, it is directly converted into carvone.

Pinocamphone has been reinvestigated in order to determine whether all its reactions are in accord with the constitution at present assigned to it. With bromine, it readily yields a dibromide,  $\text{C}_{10}\text{H}_{14}\text{OBr}_2$ , which is crystalline and melts at 118—119°.

When oxidised by 1 per cent. permanganate or chromic acid in acetic acid solution, a ketonic acid,  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , together with a dibasic acid,  $\text{C}_{10}\text{H}_{16}\text{O}_4$ , are produced; the ketonic acid is separated from the dibasic acid by taking advantage of its solubility in benzene, and

shown by conversion into its semicarbazone to be identical with *a*-pinonic acid. The dicarboxylic acid melts at 186—187°, and is an isomeride of camphoric acid, since by acetyl chloride it is converted into an anhydride. The course of the oxidation is shown by the following scheme:



Pinyamine can be very simply prepared by reducing nitrosopinene with zinc and acetic acid, and, after making alkaline, distilling the base in steam. It boils at 90° under 12 mm. pressure, and has a sp. gr. 0.944 and  $n_D$  1.5062 at 15°, and a sp. gr. 0.94 and  $n_D$  1.5036 at 20°. The value of the molecular refraction indicates the presence of one ethylene linking.

When oxidised with a one per cent. solution of permanganate, pinyamine does not yield pinocarveol, but carvopinone and a *monobasic acid*,  $\text{C}_9\text{H}_{14}\text{O}_3$  (?), which forms crystals melting at 89° and boils at 160—170° under 12 mm. pressure; it is not a ketonic acid, neither is it readily oxidised further by chromic acid. The absence of pinocarveol from the oxidation products of pinyamine affords further evidence for the view that, in the change of pinyamine into pinocarveol, a displacement of the linking takes place.

[With EDUARD ISAAC.]—Further attempts have been made in order to determine whether the nitro-compound obtained from pinene is a true pinene derivative. On reduction with zinc dust and acetic acid, a base,  $\text{C}_{10}\text{H}_{17}\text{N}$ , is obtained, identical with Pesci's aminoterebenthene; it boils at 95° under 12 mm. pressure, and has a sp. gr. 0.9325 and  $n_D$  1.496 at 19° for the base prepared from *d*-pinene, whilst the base obtained from *l*-pinene has a sp. gr. 0.932 and  $n_D$  1.4957 at 20°. Both specimens of the base are laevorotatory. Methylation of the base gives the compound  $\text{C}_{10}\text{H}_{15}\text{NMe}_3\text{I}$ , which melts at 198°.

When the oxalate of the base is treated with nitrous acid and the alcohol thus formed oxidised with chromic acid, a compound with an odour of cuminaldehyde is produced; it yields a semicarbazone melting at 201—203°, and is oxidised by chromic acid to cuminic acid (m. p. 115°). From these facts it is deduced that the base aminoterebenthene has the amino-group in the side-chain, probably having the

constitution represented by the formula  $\text{CH}_2 \begin{array}{l} \diagup \text{CH} \cdot \text{C}(\text{CH}_2 \cdot \text{NH}_2) \\ \diagdown \text{CH} - \text{CH}_2 \end{array} \begin{array}{l} \diagup \text{CMe}_2 \\ \diagdown \end{array} \text{CH}.$   
K. J. P. O.

**Essential Oil of Rue.** HENRI CARETTE (*J. Pharm. Chim.*, 1906, [vi], 24, 58—62. Compare Power and Lees, *Trans.*, 1902, 81, 1585).—The “summer oil of rue” from Algeria, prepared from *Ruta montana*, is very similar to the oil of rue prepared from *Ruta graveolens*, solidifying at 5—8° and consisting principally of methyl nonyl



ketone. Algerian "winter oil of rue," however, is obtained from *Ruta bracteosa*, solidifies at  $-15^{\circ}$  to  $-18^{\circ}$ , and consists almost entirely of methyl heptyl ketone; Corsican "oil of rue" is similar, being also obtained from *Ruta bracteosa*. W. A. D.

Correction. OSSIAN ASCHAN (*Ber.*, 1906, 39, 2596).—In a previous paper on the terpenes of Finnish pines and firs (this vol., i, 442), *Pinus sylvestris* and *P. abies* were incorrectly referred to as the Finland pine and the Finland fir respectively; it should have been the reverse. C. S.

Swedish Turpentine Oil. IWAN L. KONDAKOFF and IWAN SCHINDELMEISER (*Chem. Zeit.*, 1906, 30, 722—723).—From a sample of Swedish turpentine oil, the authors have isolated *p*-cymene and a small quantity of a hydrocarbon boiling at  $145^{\circ}$ , which they imagine to be either styrene or toluene. P. H.

Elemi Resins. V. ALBERT VESTERBERG (*Ber.*, 1906, 39, 2467—2472. Compare Abstr., 1887, 733; 1891, 165; 1892, 289, 290).—From Manilla elemi, Baup isolated (*Jahresb. Chem.*, 1851, 528), in addition to amyirin, three other crystalline substances, brein, breidin, and bryoidin. The author has separated into two substances, by crystallisation from benzene, the residue in the alcoholic mother liquor from which amyirin has been crystallised. Of these two substances, the one forms colourless, transparent tablets, melts at  $216-217^{\circ}$ , and appears to be Baup's brein; the other forms thick yellow prisms and melts at  $170-180^{\circ}$ . Both, however, give the same acetate,  $C_{30}H_{48}(OAc)_2$ , which melts at  $196^{\circ}$ , evolves hydrogen bromide on treatment with bromine, and does not give an iodine number.

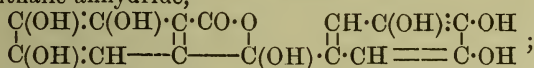
Brein,  $C_{30}H_{48}(OH)_2$  (?), separates from benzene in deliquescent leaflets containing  $2C_6H_6$ , and from alcohol in small prisms, has  $[\alpha]_D^{25}$   $65.5^{\circ}$  at  $15.5^{\circ}$  in alcoholic solution, gives a clear yellow liquid with Liebermann's cholesterol reagent, is not affected by sodium and amyl alcohol, and is probably closely related to amyirin, although it is not identical with oxyamyirin. C. S.

Colouring Matter in Saffron. F. DECKER (*Chem. Zeit.*, 1906, 30, 705).—The potassium or sodium salts of crocetin are obtained by adding alcoholic potassium or sodium hydroxide to a solution of crocetin in dilute aqueous potassium or sodium hydroxide until no further precipitate is formed; on warming the respective solutions, the precipitates dissolve, and are deposited on cooling in crystalline form, the potassium salt in nodular aggregates and the sodium salt in needles. P. H.

Constitution of Tannin. J. DEKKER (*Ber.*, 1906, 39, 2497—2502).—A specimen of commercial tannin had  $[\alpha]_D^{25} + 65^{\circ}$ ; when boiled with dilute sulphuric acid, in one hour 51.3 per cent., in two hours 73.4 per cent., and in six hours 74 per cent. of the tannin was converted

into gallic acid, the resulting solutions having  $[\alpha]_D + 22^\circ$ ,  $+ 7^\circ$ , and  $+ 6^\circ$  respectively.

The author considers that tannin must be represented as a derivative of phthalic anhydride,



this constitution is in accordance with the optical activity, the almost complete hydrolysis to gallic acid, the formation of diphenylmethane on distillation with zinc dust (Nierenstein, Abstr., 1905, i, 914), the formation of a hexamethyl derivative (Herzig and Tscherne, Abstr., 1905, i, 354), and the absence of a carboxyl group as shown by Boettinger (Abstr., 1884, 318) and by Walden (Abstr., 1899, i, 212).

Hexa-acetyltannin is formed, together with triacetyl gallic acid, by boiling tannin with acetic anhydride and sodium acetate; it melts at  $129^\circ$  and has  $[\alpha]_D + 64.4^\circ$ . G. Y.

### Valency of the Oxygen Atom in Xanthyl Compounds.

**Double Salts of Xanthyl and Metallic Haloids.** ROBERT FOSSE and L. LESAGE (*Compt. rend.*, 1906, 142, 1543—1545. Compare Abstr., 1905, i, 541, 917).—The author has prepared the following double salts of xanthyl (xanthonium) and metallic haloids: *xanthyl*

*platinichloride*,  $\text{PtCl}_4 \cdot 2\text{RCl}$  [where R represents  $\text{CH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{O}-$ ], an orange powder; *xanthyl platinibromide*,  $\text{PtBr}_4 \cdot 2\text{RBr}$ , an orange-yellow precipitate; *xanthyl aurichloride*,  $\text{AuCl}_3 \cdot \text{RCl}$ , microscopic, yellow crystals; *xanthyl auribromide*,  $\text{AuBr}_3 \cdot \text{RBr}$ , small, brick-red crystals; *xanthyl uranylchloride*,  $\text{UO}_2\text{Cl}_2 \cdot 2\text{RCl}$ , golden-yellow, prismatic crystals; *xanthyl uranyl bromide*,  $\text{UO}_2\text{Br}_2 \cdot 2\text{RBr}$ , yellow crystals; *xanthyl ferribromide*,  $\text{FeBr}_3 \cdot \text{RBr}$ , bright red, microscopic crystals; *xanthyl zincobromide*,  $\text{ZnBr}_2 \cdot 2\text{RBr}$ , orange-yellow crystals; *xanthyl copper bromide*,  $\text{CuBr}_2 \cdot 2\text{RBr}$ , small, dull violet crystals; *xanthyl cadmium bromide*,  $\text{CdBr}_2 \cdot 2\text{RBr}$ , small, yellow crystals; *xanthyl lead bromide*,  $2\text{PbBr}_2 \cdot \text{RBr}$ , small, clear brown crystals; *xanthyl mercuribromide*,  $3\text{HgBr}_2 \cdot 4\text{RBr}$ , golden-yellow crystals. M. A. W.

**Coeroxene, its Derivatives and Isologues.** HERMAN DECKER (*Annalen*, 1906, 348, 210—250. Compare Baeyer, *Ber.*, 1871, 4, 555, 658; Orndorff and Brewer, Abstr., 1900, i, 447; 1901, i, 724; Laube, this vol., i, 598).—The name coeroxene is proposed for the parent

substance,  $\begin{array}{c} \text{CH}-\text{C}_6\text{H}_3- \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{O}$ , of coerulein and coerulin, which become

trihydroxycoeroxone and tetrahydroxycoeroxenol respectively, and the names coeramidine and coerthiene for the isologous cyclic systems,

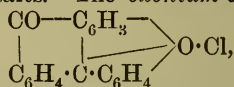
$\begin{array}{c} \text{CH}-\text{C}_6\text{H}_3- \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{NH}$  and  $\begin{array}{c} \text{CH}-\text{C}_6\text{H}_3- \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{S}$ , respectively.

[With ENOS FERRARIO].—When treated with ammonia under cooling

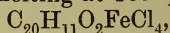
with ice, *coeroxonium sulphate*, which is prepared by the action of sulphur trioxide on fluoran dissolved in concentrated sulphuric acid below

40°, yields *coeroxonol*,  $\begin{array}{c} \text{CO} \text{---} \text{C}_6\text{H}_3 \text{---} \text{O} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_4 \end{array}$ , which is the carbinol base of

the coeroxonium salts. This separates from benzene, ether, chloroform, acetic acid, or acetone in colourless, strongly refracting prisms, becomes violet when heated with a solvent, darkens at 140—160°, and when quickly heated melts and decomposes at 179—180°; it dissolves in dilute mineral acids to form the blood-red oxonium salts, but is almost colourless in acetic acid solution; with dilute hydrochloric acid, an equilibrium is set up between the colourless carbinol, the acid, and the red oxonium salt. When boiled with absolute alcohol, the carbinol forms the *ethyl ether*,  $\text{C}_{22}\text{H}_{16}\text{O}_3$ , which separates in small, violet, shimmering crystals, melts at 145—146°, and is converted by acids into the oxonium salts. The *oxonium chloride*,



crystallises in red needles melting at 185°; the *ferrichloride*,



melts at 233°; the *mercurichloride* melts and decomposes at 228°; the *platinichloride*,  $(\text{C}_{20}\text{H}_{11}\text{O}_2)_2\text{PtCl}_6$ , commences to decompose at 315°; the *bromide*,  $\text{C}_{20}\text{H}_{11}\text{O}_2\text{Br}$ , forms red needles and melts at about 115°; the *tribromide*,  $\text{C}_{20}\text{H}_{11}\text{O}_2\text{Br}_3$ , forms a scarlet precipitate and loses bromine in a desiccator; the *iodide*,  $\text{C}_{20}\text{H}_{11}\text{O}_2\text{I}$ , melts at 216° and is very sparingly soluble; the *picrate*, *chromate*, and *nitrate* also were prepared.

3 : 13-*Dimethylcoeroxonium sulphate* is formed by the action of sulphur trioxide on dimethylfluoran in sulphuric acid solution; the *carbinol*

base,  $\begin{array}{c} \text{CO} \text{---} \text{C}_6\text{H}_2\text{Me} \text{---} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3\text{Me} \end{array} \text{---} \text{O}$ , melts at 152°; the *ferrichloride*,  $\text{C}_{22}\text{H}_{15}\text{O}_2\text{FeCl}_4$ , melts at 160°.

*Coeroxenol*,  $\begin{array}{c} \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3 \text{---} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \text{---} \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{---} \text{O}$ , is prepared by the reduction of

coeroxonol in alcoholic alkaline solution, or of coeroxonium salts in acid solution by means of zinc dust, stannous chloride, or hydriodic acid, or by heating phenylxanthenecarboxylic acid with concentrated sulphuric acid at 100°. It crystallises in yellowish-green plates, melts at 136°, dissolves in aqueous alkali hydroxides forming a red, in acetic acid forming a yellow solution with yellow fluorescence, is readily oxidised by air to coeroxonol or coeroxonium salts, and gives a red coloration and green fluorescence in concentrated sulphuric acid. The *acetyl* derivative,  $\text{C}_{22}\text{H}_{14}\text{O}_3$ , formed by reduction of coeroxonol in a solution containing acetic anhydride, crystallises in dark yellow leaflets, melts at 212°, is not oxidised by air, and is hydrolysed only slowly by boiling alcoholic sodium hydroxide.

*Coeroxene*,  $\text{C}_{20}\text{H}_{12}\text{O}$ , formed by boiling coeroxenol with hydriodic acid of sp. gr. 1.6 and phosphorus, crystallises in yellow leaflets, melts



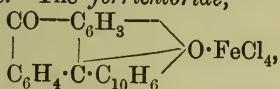
at  $153^{\circ}$ , is readily soluble in chloroform, benzene, or light petroleum, forming solutions with intense yellowish-green fluorescence, and with sulphuric acid gives a red coloration, becoming violet on heating; it is insoluble in aqueous sodium hydroxide and is not oxidised by air, but on treatment with arsenic, nitric, or chromic acid in glacial acetic acid solution forms coeroxonium salts. It is probably identical with R. Meyer and Saul's compound, formed by distilling fluoran with zinc dust (Abstr., 1893, i, 220).

[With MATEI SASSU.]—10-Phenylcoeroxene,  $\begin{array}{c} \text{CPh}-\text{C}_6\text{H}_3- \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{O}$ , pre-

pared by the action of magnesium phenyl bromide on coeroxonol ethyl ether, is orange-red, melts at  $188^{\circ}$ , at higher temperatures forms a fluorescent vapour, gives an orange coloration with sulphuric acid, and is stable towards feeble oxidising agents, but is oxidised, becoming scarlet, by lead dioxide or chromic or sulphuric acid in hot glacial acetic acid solution.

[With EDUARD LAUBE.]—1-Phenoxyanthraquinone, melting at  $145^{\circ}$ , is oxidised by sulphur trioxide in sulphuric acid solution at  $160-180^{\circ}$ , forming coeroxonium sulphate.

1- $\beta$ -Naphthoxyanthraquinone,  $\text{C}_{24}\text{H}_{14}\text{O}_3$ , prepared by fusing  $\beta$ -naphthol with sodium  $\alpha$ -anthraquinonesulphonate and potassium hydroxide at  $170-180^{\circ}$ , forms small, yellow crystals, melts at about  $180^{\circ}$ , gives with concentrated sulphuric acid an olive-green coloration, becoming scarlet at  $100^{\circ}$ , and when heated with 65—70 per cent. sulphuric acid at  $130-150^{\circ}$  is converted into  $\beta$ -benzocoeroxonium sulphate, which is only sparingly soluble. The *ferrichloride*,



is obtained as a black, crystalline precipitate, which melts and decomposes at  $240^{\circ}$ , and becomes blood-red when heated with concentrated sulphuric acid at  $100^{\circ}$ . The *chloride* and *nitrate* form red needles; the *iodide* is obtained as a dark violet, crystalline powder; the *platinichloride* is scarlet.

$\beta$ -Benzocoeroxonol,  $\begin{array}{c} \text{CO}-\text{C}_6\text{H}_3-\text{O} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_{10}\text{H}_6 \end{array}$ , is readily oxidised by air; the *ethyl ether*,  $\text{C}_{26}\text{H}_{18}\text{O}_3$ , forms almost colourless crystals and melts at  $193-194^{\circ}$ .  $\beta$ -Benzocoeroxenol,  $\text{C}_{24}\text{H}_{14}\text{O}_2$ , is yellowish-red, forms solutions with strong yellowish-red fluorescence, and is readily oxidised by air. The *acetyl derivative*,  $\text{C}_{26}\text{H}_{16}\text{O}_3$ , forms yellowish-brown crystals, melts at  $206^{\circ}$ , and is hydrolysed on prolonged boiling with alcoholic sodium hydroxide. When reduced with concentrated hydriodic acid,  $\beta$ -benzocoeroxonium salts yield  $\beta$ -benzocoeroxene, which is strongly fluorescent and is insoluble in aqueous alkali hydroxides.

$\alpha$ -Benzocoeroxonium sulphate is formed by oxidation of 1- $\alpha$ -naphthoxyanthraquinone, melting at  $275-276^{\circ}$ . The members of this series closely resemble the derivatives of  $\beta$ -benzocoeroxene.

[With AUGUST WUERSCH.]—1-Phenylthioanthraquinone,  $\text{C}_{14}\text{H}_7\text{O}_2 \cdot \text{SPh}$ , prepared by heating thiophenol with potassium hydroxide and potassium

$\alpha$ -anthraquinonesulphonate at  $170^\circ$ , crystallises in long, yellow needles, melts at  $185^\circ$ , dissolves in concentrated sulphuric acid, forming a dark green solution, and yields 1-hydroxyanthraquinone when heated with dilute alkali hydroxides. When heated with 70 per cent. sulphuric acid at  $160^\circ$ , it is converted into the sparingly soluble, dark violet *coerthionium sulphate*. *Coerthionium ferrichloride*,  $C_{20}H_{11}OSFeCl_4$ , forms dark violet crystals, melts and decomposes at  $227^\circ$ , and is decomposed by water. The colour of these thionium salts is darker and more intense than that of the coeroxonium salts.

*Coerthionol*,  $\begin{array}{c} \text{CO} \text{---} \text{C}_6\text{H}_3 \text{---} \text{S} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_4 \end{array}$ , crystallises in slightly yellow prisms, melts at  $220^\circ$ , and dissolves in dilute acids, forming violet solutions.

*Coerthienol*,  $\begin{array}{c} \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3 \text{---} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \text{---} \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{S}$ , formed by reduction of coerthionol, is yellow, dissolves in ether or alcohol, forming a solution with intense green fluorescence, and is readily oxidised to coerthionium salts.

[With CARL SCHENK.]—Coeramidonine (Damman and Gattermann, Abstr., 1902, i, 795), melting at  $206^\circ$ , is formed in good yield by heating *o*-acridylbenzoic acid with fuming sulphuric acid; it dissolves in concentrated sulphuric acid to a blood-red, in glacial acetic acid to a yellow, or in pyridine to a golden solution. *Coeramidonium platinichloride*,  $C_{40}H_{24}O_2N_2PtCl_6$ , forms glistening, red crystals and melts at  $260^\circ$ ; the *picrate*,  $C_{26}H_{14}O_8N_4$ , forms red crystals and melts at  $241^\circ$ . The *methosulphate* of *N*-methylcoeramidonium, formed by the action of methyl sulphate on coeramidonine, crystallises in small, red leaflets and dyes cotton wool mordanted with tannin a brownish-red, fast to soap. The *picrate*,  $C_{27}H_{16}O_8N_4$ , forms red

crystals and melts at  $208^\circ$ ; the *methiodide*,  $\begin{array}{c} \text{CO} \text{---} \text{C}_6\text{H}_3 \text{---} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{N:MeI}$ , crystallises in brownish-red needles and melts and evolves methyl iodide at  $218^\circ$ ; the *nitrate* melts at  $188$ — $189^\circ$ .

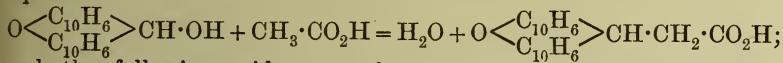
*N*-Methylcoeramidonol,  $\begin{array}{c} \text{CO} \text{---} \text{C}_6\text{H}_3 \text{---} \text{NMe} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_4 \end{array}$ , formed by treatment of the quaternary salts with sodium hydroxide, is obtained as a voluminous precipitate, crystallises from alcohol, and melts at  $126^\circ$ . The *ethyl* ether forms small plates and melts at  $152^\circ$ ; the *methyl* ether crystallises in small, deep brown leaflets with metallic lustre and melts at  $155^\circ$ .

[With ENOS FERRARIO.]—Coeramidonium salts are formed also by the action of fuming sulphuric acid on the acridine derivatives described by Decker and Hock (Abstr., 1904, i, 450).

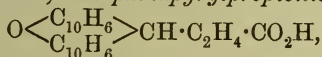
[With MATEI SASSU.]—*Coeramidenol*,  $\begin{array}{c} \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3 \text{---} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \text{---} \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{NH}$ , is prepared by reduction of coeramidonine in acid, neutral, or alkaline solution; it forms a dark red solution with reddish-yellow fluorescence in ether or benzene, is soluble in aqueous alkali hydroxides, but insoluble

in dilute sulphuric acid, and is readily oxidised by air. The *acetyl* derivative,  $C_{22}H_{15}O_2N$ , forms dark red crystals, melts at  $254^\circ$ , has an intense yellow fluorescence in solution, and is hydrolysed by boiling aqueous alkali hydroxides. G. Y.

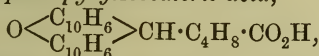
**A Reaction of some Acid Anhydrides. New Series of Acids containing the Pyran Ring.** ROBERT FOSSE (*Compt. rend.*, 1906, 143, 59—61).—Dinaphthapyranol and xanthidrol react with certain acid anhydrides with the elimination of water and the formation of the corresponding substituted acid; thus dinaphthapyranol and acetic anhydride give dinaphthapyrylacetic acid according to the equation



and the following acids were thus prepared: *dinaphthapyrylacetic acid*,  $O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CH\cdot CH_2\cdot CO_2H$ , forms beautiful, colourless crystals melting at  $194^\circ$  and yields crystalline *silver*, *potassium*, *sodium*, *barium*, and *calcium* salts; *dinaphthapyrylpropionic acid*,



forms colourless crystals which melt at  $197^\circ$ ; *dinaphthapyryl- $\alpha$ -isobutyric acid*,  $O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CH\cdot C_3H_6\cdot CO_2H$ , forms colourless crystals melting at  $221^\circ$ ; *dinaphthapyrylisovaleric acid*,



forms colourless crystals which melt and decompose at  $208-210^\circ$ ;

*dinaphthapyrylsuccinic acid*,  $O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$ ,

forms beautiful, colourless crystals which melt and decompose at

$225-230^\circ$ ; *xanthylacetic acid*,  $O\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle CH\cdot CH_2\cdot CO_2H$ , crystallises

in beautiful, colourless needles which melt at  $155.5-156^\circ$ , can be sublimed, and is soluble in alcohol and slightly so in boiling water; and

*xanthylisovaleric acid*,  $O\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle CH\cdot C_4H_8\cdot CO_2H$ , forms colourless crystals which melt at  $147-150^\circ$ .

M. A. W.

**Stable Derivatives of the Active Base of the Extract of Suprarenal Glands.** FARBERGE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 167317).—When one mol. of the active base of the suprarenal glands is combined in aqueous solution with either boric acid (1.5 mols.) or one of its aryl derivatives (phenylboric or *m*-tolylboric acid), a stable soluble salt is produced which, on evaporation, is left as a brittle, vitreous mass having the composition  $C_{18}H_{27}O_{11}N_2B_3$ ; when precipitated with alcohol, the salt contains one  $H_2O$  less, but both preparations have the same physiological action. The salts with phenyl- and *m*-tolyl-boric acids are pale yellow powders having similar properties. These compounds may be heated to  $250^\circ$



without decomposition, and they all give a violet coloration with ferric chloride, which changes to green when this reagent is added in excess.

G. T. M.

*iso*Coniine and the Synthesis of Coniine. ALBERT LADENBURG (*Ber.*, 1906, 39, 2486—2491. Compare Abstr., 1893, i, 442; 1897, i, 173; Wolfenstein, Abstr., 1894, i, 627; 1895, i, 253; 1896, i, 631).—Attempts to obtain *iso*coniine as an individual substance have been unsuccessful, but it has undoubtedly a higher rotatory power than coniine. The fact that synthetic coniine has a greater rotatory power than the purest natural *d*-coniine is probably due to the presence of *iso*coniine in the former. The author has therefore repeated his former experiments and has shown that synthetic coniine is isomeric with *d*-coniine, being identical with it in most of its properties, but having a greater rotatory power, about 4°. It boils at 167° (corr.) and has a sp. gr. 0.8472 at 17° and 0.8445 at 20°; the anhydrous bitartrate melts at 54—55°, the hydrochloride at 221—222°, and the anhydrous. platinichloride at 174°. In order to complete the synthesis of *d*-coniine it is necessary to heat the synthetic product for many hours at 290°, when pure *d*-coniine is obtained, having  $[\alpha]_D^{15.67}$  at 21°.

The allylpyridine required in the synthesis is obtained by heating *a*-picoline, aldehyde, and water at 150°; the resulting aldol compound,  $C_5NH_4 \cdot CH_2 \cdot CHMe \cdot OH$ , is heated with concentrated hydrochloric acid at 185°, whereby a mixture of allylpyridine and chloropropylpyridine is obtained, which is reduced to *i*-coniine by sodium and absolute alcohol.

C. S.

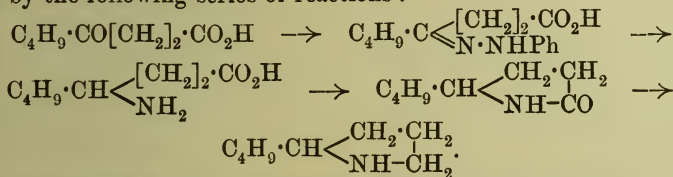
[*apo*Morphine Salts.] J. D. RIEDEL (D.R.-P. 167879. Compare Pschorr, Abstr., 1905, i, 658).—*apo*Morphine methobromide, methochloride, and methonitrate may be produced by adding saturated aqueous solutions of potassium bromide, chloride, and nitrate respectively to the syrupy product of the action of methyl sulphate on *apomorphine* in ethereal solution; the methobromide, which at first is viscid, is rendered crystalline by dissolving in methyl alcohol and precipitating from this solution with acetone.

G. T. M.

Soluble Double Salt of Sodium Salicylate and Barium Theobromine. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 167140).—Two mols. of sodium salicylate added to a mixture of sodium theobromine (2 mols.) and barium salicylate (1 mol.) in aqueous solution give rise to a soluble *double salt* which separates on concentrating the solution under diminished pressure. G. T. M.

The Relations between Functional (Reactive) Groups in Remote Positions. Cyclic Imines. EDMOND E. BLAISE and HOUILLON (*Compt. rend.*, 1906, 142, 1541—1543).—The existence of decamethyleneimine (compare Phookan and Krafft,

Abstr., 1892, 1180) affording evidence in favour of the view that there exists a periodicity in the closing of heterocyclic chains, the authors attempted to prepare octomethyleneimine by the action of heat on octomethylenediamine hydrochloride. The product obtained by this reaction was a 2-butylpyrrolidine,  $C_4H_9 \cdot CH \begin{smallmatrix} \text{NH} \text{---} \text{CH}_2 \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix}$ , which has an odour closely resembling that of coniceine and boils at the same temperature as *i*-coniceine; the *platinichloride* melts at  $123^\circ$ , the *aurichloride* at  $89^\circ$ , and the *carbamide* at  $152^\circ$ . 2-Butylpyrrolidine prepared as above is identical with the synthetical compound obtained from  $\beta$ -butyrylpropionic acid [ $\delta$ -propyl-lævulic acid or  $\gamma$ -keto-octoic acid] by the following series of reactions:



In view of the fact that octomethylenediamine hydrochloride on heating suffers an intramolecular migration with the formation of a pyrrolidine base, the authors suggest that Phookan and Krafft's (*loc. cit.*) decamethyleneimine is probably 2-hexylpyrrolidine.

M. A. W.

**Constitution of Hæmopyrrole.** WILLIAM KÜSTER [with KARL HAAS] (*Annalen*, 1906, 346, 1—27).—Since hæmatin on oxidation yields a substituted maleimide, it was to be expected that hæmopyrrole would yield an acid amide from the nature of which the constitution of hæmopyrrole could be deduced. Recent investigation of hæmatic acid (Küster) appears to show that hæmopyrrole is either methylpropylpyrrole or 3:4-diethylpyrrole, or possibly a mixture of the two.

The oxidation of hæmopyrrole yielded no definite results, although the products resembled a di-substituted maleimide and gave a barium salt similar to barium methylethylmaleate. A crystalline imide, soluble in ether and melting at  $63^\circ$ , was also isolated; methylpropylmaleimide melts at  $56\text{--}57^\circ$ . Hydrolysis of the imide yielded an oily anhydride, resembling in odour a disubstituted maleic anhydride; but the substance could not be purified.

*Methylpropylmaleic anhydride*,  $C_8H_{10}O_3$ , is prepared by treating ethyl propylacetoacetate in ethereal solution with an aqueous solution of potassium cyanide and hydrochloric acid; the methylpropylmalic acid which is obtained by hydrolysing the product is then heated with acetic anhydride at  $240^\circ$ ; the anhydride is an oil boiling at  $241\text{--}242^\circ$  (corr.) under 760 mm. pressure and has a sp. gr. 1.098 at  $15^\circ$ , and  $K = 0.0073$ . Of the corresponding acid, which could not be isolated, the *barium*, *strontium*, and *calcium* salts crystallise in leaflets with  $H_2O$ ; the *copper* salt and *silver* salts are anhydrous and amorphous.

The *ethyl* ester prepared from the silver salt is an oil decomposing at  $190^{\circ}$ . An *ammonium* salt of the methylpropylmaleamide,  $C_8H_{16}O_3N_2$ , is formed when dry ammonia is passed into an ethereal solution of the anhydride.

*Methylisopropylmaleic anhydride*, prepared similarly to the compound last described from ethyl isopropylacetoacetate, is a pale yellow oil, boiling at  $240$ — $242^{\circ}$ . The *barium* salt of the corresponding acid,  $C_8H_{10}O_4Ba \cdot H_2O$ , crystallises in leaflets, the *copper* and *silver* salts are amorphous. Xeronic acid,  $\begin{matrix} \text{CET} \cdot \text{CO} \\ | \\ \text{CET} \cdot \text{CO} \end{matrix} > \text{O}$ , was prepared by distilling citraconic acid rapidly at  $200^{\circ}$ ; its boiling point was found to be  $239$ — $240^{\circ}$ .

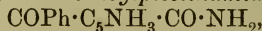
*Methylpropylmaleimide*, prepared by heating the anhydride with alcoholic ammonia at  $130^{\circ}$ , crystallises in needles melting at  $56$ — $57^{\circ}$ . The corresponding *isopropyl compound* is prepared in a similar manner, and is a pale yellow, crystalline solid melting at  $44$ — $45^{\circ}$ . Attempts to prepare the corresponding xeronimide did not lead to the formation of a crystalline product.

The reduction of methylpropylmaleic anhydride with zinc dust and acetic acid led to the formation of the fumaroid methylpropylsuccinic acid (m. p.  $156$ — $158^{\circ}$ ); reduction with sodium or aluminium amalgam in acid solution gave the same result. The corresponding *methylisopropylsuccinic acid* is obtained from the corresponding anhydride; it sinters at  $165^{\circ}$  and melts at  $171^{\circ}$ .

On reducing hæmin with hydriodic acid in acetic acid solution, hæmopyrrole is formed and isolated by distillation in steam. The distillate is immediately oxidised with chromic acid, and the product isolated by extraction with ether after neutralisation with sodium carbonate. Finally a crystalline substance containing nitrogen was isolated; it melted at  $63$ — $64^{\circ}$ . The alkaline liquor, which had been extracted with ether, contained a substance melting at  $93$ — $96^{\circ}$  which had all the properties of hæmatic acid.

K. J. P. O.

**3-Benzoylpicolinic Acid.** ALFRED KIRPAL (*Monatsh.*, 1906, 27, 371—377. Compare Bernthsen and Mettegang, *Abstr.*, 1887, 737; Meyer, this vol., i, 358).—3-Benzoylpicolinamide,



is formed from the acid by treatment with thionyl chloride and careful addition of the resulting acid chloride to strongly cooled, aqueous ammonia; it crystallises in quadratic plates, melts at  $175^{\circ}$ , and is hydrolysed only slowly by boiling water. 2-Amino-3-benzoylpyridine,  $\text{NH}_2 \cdot C_5\text{NH}_3 \cdot \text{COPh}$ , prepared by the action of bromine on the amide in sodium hydroxide solution, crystallises in yellow needles, melts at  $145^{\circ}$ , and when boiled with sodium nitrite in dilute sulphuric acid solution yields 2-hydroxy-3-benzoylpyridine,  $\text{OH} \cdot C_5\text{NH}_3 \cdot \text{COPh}$ ; this is formed also by heating 2-hydroxynicotinyl chloride with benzene and aluminium chloride. It crystallises in colourless needles, melts at  $149^{\circ}$ , and gives a rose coloration with aqueous ferric sulphate.

2-Hydroxynicotinyl chloride,  $\text{OH} \cdot C_5\text{NH}_3 \cdot \text{COCl}$ , prepared by the action

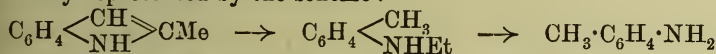


of thionyl chloride on the acid, crystallises in short, yellow needles, melts and decomposes at  $225^{\circ}$ , and loses hydrogen chloride, forming the *anhydride*, on prolonged heating at  $100^{\circ}$ .

*Methyl 2-hydroxynicotinate*,  $C_6H_4O_3NMe$ , prepared by the action of methyl alcohol on the acid chloride or by boiling the acid with methyl alcohol and a few drops of concentrated sulphuric acid, crystallises from benzene in colourless needles and melts at  $153^{\circ}$ . G. Y.

**Formation and Decomposition of the Indole Nucleus by the Catalytic Action of Nickel.** ORESTE CARRASCO and MAURICE PADOA (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 699—703. Compare this vol., i, 530).—At temperatures up to about  $200$ — $250^{\circ}$ , and in presence of hydrogen, finely-divided nickel acts as a hydrogenating agent, whilst at higher temperatures the same catalytic agent tends towards dehydrogenation, even when hydrogen itself is present.

Thus, when a mixture of hydrogen and indole vapour is passed over reduced nickel maintained at about  $200^{\circ}$ , the indole undergoes reduction and loses a carbon atom, forming *o*-toluidine. Under similar conditions, 2-methylindole also yields *o*-toluidine, the changes being probably represented by the scheme :

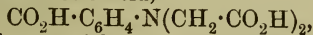


On the other hand, when the vapour of methyl-*o*-toluidine is passed over finely-divided nickel heated at  $300$ — $330^{\circ}$ , it undergoes de-methylation and gives rise to indole ; no indoline is formed in this reaction.

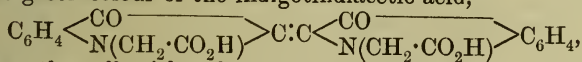
T. H. P.

**Preparation of Indoxyl and its Homologues.** LÉON LILIENFELD (D.R.-P. 166447).—The aromatic glycines when condensed with the alkali hydroxides furnish only a very poor yield of indoxyl. An intimate mixture of potassium glycinate with dry potassium hydroxide and calcium hydroxide or magnesia is heated at  $150$ — $300^{\circ}$  in a current of ammonia. The yield of indoxyl is in this way increased from 10 to 35 or 40 per cent., depending on the way in which the gas is introduced into the fused mass ; the more intimate the mixing the higher the yield. G. T. M.

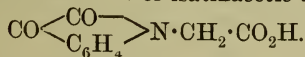
**Preparation of Indoxyl.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 168292).—Anthranilodiacetic acid,



is heated for twelve hours with strong sodium hydroxide solution, the mixture then diluted considerably, and oxidised by a current of air until the green colour of the indigotindiacetic acid,



changes to the yellowish-red tint of isatinacetic acid,



The last of these compounds is converted into phenylglycine-*o*-carboxylic acid when the solution is evaporated, the product separating in

the form of its sodium salt, which can be used in preparing indoxyl and indigotin. G. T. M.

**Constitution of the Indole Group in Albumin. III Oxidation of Tryptophan to Indole-3-aldehyde.** ALEXANDER ELLINGER (*Ber.*, 1906, **39**, 2515—2522. Compare Abstr., 1904, i, 639, 1905, i, 827).—It follows from the constitution of Nencki's scatole-acetic acid (indole-3-propionic acid) that tryptophan must be scatole-3- $\alpha$ -aminopropionic,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{---CH} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , or scatole-

3- $\beta$ -aminopropionic acid,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{---CH} \end{smallmatrix} \text{C} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

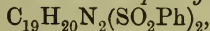
When oxidised by Hopkins and Cole's method (Abstr., 1903, i, 590), tryptophan yields *indole-3-aldehyde*,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{---CH} \end{smallmatrix} \text{C} \cdot \text{COH}$ , which crystallises in colourless plates, melts at  $195^\circ$ , and when heated with 20 per cent. sulphuric or hydrochloric acid forms a red *dye*; this crystallises in needles, melts at about  $175^\circ$ , and gives a characteristic absorption spectrum resembling, but not identical with, that of the scatole dye from urine. The aldehyde interacts with hippuric acid, sodium acetate, and acetic anhydride, forming an azlactone (compare Erlenmeyer, jun., Abstr., 1902, i, 595), and when oxidised with permanganate in alkaline solution yields indole-3-carboxylic acid.

The action of chloroform and potassium hydroxide in alcoholic solution on indole leads to the formation of indole-3-aldehyde and 3-chloroquinoline (Edinger, Abstr., 1897, i, 103), which boils at  $141^\circ$  under 15 mm. pressure and yields an *aurichloride*,  $\text{C}_9\text{NH}_6\text{Cl} \cdot \text{HAuCl}_4$ , melting at  $173^\circ$ . G. Y.

**Action of Formaldehyde (Methanal) on Tetrahydroquinoline.** R. A. WEERMAN (*Rec. trav. chim.*, 1906, **25**, 260—270).—Formaldehyde and tetrahydroquinoline readily condense at the ordinary temperature or on warming to form a yellow oil which probably contains the *aminoalcohol*,  $\text{C}_9\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{OH}$ , for on treatment with hydrogen cyanide it yields the *nitrile*,  $\text{C}_9\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CN}$ , in the form of a colourless, thick oil, which boils at  $193$ — $195^\circ$  under 7 mm. pressure, and is saponified by means of an alcoholic solution of sodium hydroxide to form *tetrahydroquinolinoacetamide*,  $\text{C}_9\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , which crystallises from alcohol in white needles melting at  $153$ — $154^\circ$ . Tetrahydroquinolinoacetoneitrile can also be prepared by the method of Knoevenagel (Abstr., 1904, i, 989), by heating a mixture of tetrahydroquinoline, formaldehyde, and sodium hydrogen sulphite, and treating the resulting crystalline acid with potassium cyanide.

If the yellow oil obtained by the condensation of tetrahydroquinoline and formaldehyde is kept, it becomes crystalline, and the chief product is *di-1-tetrahydroquinolylmethane*,  $\text{CH}_2(\text{C}_9\text{NH}_{10})_2$ , which crystallises from ether or light petroleum in large, rhombic prisms melting at  $61$ — $62^\circ$ , and is converted by the action of mineral acids into the isomeride *di-6-tetrahydroquinolylmethane*,  $\text{CH}_2(\text{C}_9\text{NH}_{10})_2$ ; this base crystallises from ether or absolute alcohol in yellow needles,

and melts at  $130^{\circ}$ , the *hydrochloride*,  $C_{19}H_{22}N_2 \cdot 2HCl$ , melts and decomposes at  $255^{\circ}$ , and the *benzenesulphonyl* derivative,

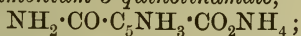


crystallises from alcohol or acetone in needles and melts at  $185-186^{\circ}$ . In addition to ditetrahydroquinolylmethane there is also formed a small quantity of a third *isomeride*,  $C_{19}H_{22}N_2$ , which is sparingly soluble in ether and forms thin, prismatic needles, which melt at  $120^{\circ}$  and yield formaldehyde when heated with dilute sulphuric acid; its constitution is at present undetermined.

M. A. W.

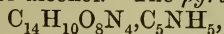
**Quinolinic Esters.** ALFRED KIRPAL (*Monatsh.*, 1906, 27, 363—369. Compare Abstr., 1900, i, 51; 1901, i, 227; Wegscheider, Abstr., 1898, i, 30).—The mother liquor from the preparation of 2-methyl-3-hydrogen quinoline by the action of methyl alcohol on the anhydride, contains a very small quantity of 3-methyl-2-hydrogen quinoline,  $CH:CH \cdot C \cdot CO_2Me$   
 $CH:N-C \cdot CO_2H$ ; this crystallises from benzene in colourless, transparent, rhombic plates [ $a:b:c = 0.5928:1:0.5869$ ], melts at  $106^{\circ}$ , and decomposes, forming carbon dioxide and ethyl nicotinate, at  $120^{\circ}$ . It is readily soluble in the ordinary solvents, is hydrolysed only very slowly by boiling water, and forms a *copper* salt crystallising in violet-blue prisms and closely resembling copper nicotinate. A table is given showing the reactions of picolinic and nicotinic acids and of 3-methyl-2-hydrogen and 2-methyl-3-hydrogen quinolinates with a number of metallic salts.

3-Methyl-2-hydrogen quinoline dissolves in concentrated aqueous ammonia, forming *ammonium 3-quinolinamate*,



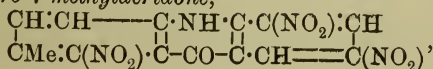
the *acid*,  $C_7H_6O_3N_2$ , crystallises in colourless prisms and melts at  $160^{\circ}$ , losing ammonia and forming *quinolinimide*, melting at  $230^{\circ}$ . G. Y.

**1:3:6-Trinitro-7-methylacridone.** SALVATORE CUTTITTA (*Gazzetta*, 1906, 36, i, 325—332).—2-*o*-Nitro-*p*-toluidino-3:5-dinitrobenzoic acid,  $CO_2H \cdot C_6H_2(NO_2)_2 \cdot NH \cdot C_6H_3Me \cdot NO_2$ , prepared by the action of alcoholic ammonia on a mixture of 2-chloro-3:5-dinitrobenzoic acid (1 mol.) and *o*-nitro-*p*-toluidine (1 mol.), crystallises from aqueous alcohol with  $2\frac{1}{2}H_2O$  in shining, lemon-yellow plates melting at  $232^{\circ}$  and dissolves sparingly in water or acetic acid and, to a less extent, in benzene. The *ammonium* salt forms golden-yellow laminae melting at  $220^{\circ}$  and dissolves in water, benzene, alcohol, or xylene. The *sodium* salt ( $+2\frac{1}{2}H_2O$ ) forms small, orange-red, triclinic crystals [F. RANFALDI:  $a:b:c = 1.52579:1:0.94494$ ;  $\alpha = 76^{\circ}11'$ ;  $\beta = 81^{\circ}27'$ ;  $\gamma = 93^{\circ}29'$ ], readily soluble in water or alcohol. The *pyridine* salt,



separates from alcohol in shining, brick-red, triclinic crystals with blue reflex [F. RANFALDI:  $a:b:c = 1.35414:1:1.09430$ ;  $\alpha = 87^{\circ}16'$ ;  $\beta = 76^{\circ}36'$ ;  $\gamma = 92^{\circ}14'6''$ ], which melt at  $200^{\circ}$  and dissolve sparingly in benzene or water.

1:3:6-Trinitro-7-methylacridone,





prepared by the action of concentrated sulphuric acid on 2-*o*-nitro-*p*-toluidino-3:5-dinitrobenzoic acid, crystallises from acetic acid in shining, yellow plates melting at 320° and dissolves sparingly in benzene or ether and readily in xylene. Its *sodium* salt ( $+2\frac{1}{2}\text{H}_2\text{O}$ ) crystallises from alcohol in minute, carmine needles soluble in sodium carbonate solution and is decomposed by water in the cold; on heating, it deflagrates violently.

T. H. P.

**Transformations of the Quaternary Ammonium Hydroxides of Acridylpropionic Acid.** CARL SCHENCK (*Ber.*, 1906, 39, 2424—2427. Compare Decker and Hock, *Abstr.*, 1904, i, 450, 620).—5-Acridyl- $\beta$ -propionic acid (Volpi, *Abstr.*, 1893, i, 350) becomes brown and melts at 310°, and loses carbon dioxide when heated with zinc chloride at 250°. The *methyl* ester,  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$ , formed by boiling the acid with hydrogen chloride in methyl-alcoholic solution, melts at 95°, is hydrolysed slowly by boiling aqueous sodium hydroxide, and forms salts which are decomposed by water. The *iodide* forms orange needles and melts and decomposes at 205°; the *picrate*,  $\text{C}_{23}\text{H}_{18}\text{O}_9\text{N}_4$ , crystallises in glistening, yellow plates and melts at 222°. When heated with methyl sulphate at 120°, the *N*-atom of the methyl ester is methylated and the resulting *base* forms a quaternary *methosulphate*; this yields a quaternary *picrate*,  $\text{C}_{24}\text{H}_{20}\text{O}_9\text{N}_4$ , which crystallises from alcohol, melts at 210°, and is not decomposed by water, alcohol or sodium hydrogen carbonate.

*Ethyl 5-acridyl- $\beta$ -propionate*,  $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}$ , crystallises in long needles melts at 83°, and is more readily hydrolysed than the methyl ester. The *picrate*,  $\text{C}_{24}\text{H}_{20}\text{O}_9\text{N}_4$ , melts at 192°.

The hydrolysis of the quaternary salts of the methylacridylpropionic esters by means of aqueous sodium hydroxide leads to the formation of the colourless, crystalline *lactone*,  $\text{NMe} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} - \text{CO} \end{smallmatrix}$ , which is soluble in ether, benzene, or alcohol, and readily dissolves in water or dilute alkali hydroxides, changing into the yellow, fluorescent

*betaine*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C} \\ \diagup \quad \diagdown \\ | \quad | \\ \text{NMe} \end{smallmatrix} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ | \quad | \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$ ; the *hydrochloride*,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{NCl}$

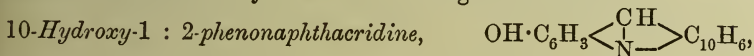
formed by dissolving the lactone in hot dilute hydrochloric acid crystallises in rosettes and melts and decomposes at 260°.

A *base*, which may be diacridylethane, is formed together with acridylpropionic acid by fusing diphenylamine with succinic acid; it forms yellow crystals, melts at about 92°, gives a yellow, fluorescent solution with concentrated sulphuric acid, and forms reddish-violet salts with mineral acids; the *picrate* melts at 113—114°. G. Y.

**Derivatives of 5-Phenylacridine. III. 5-*p*-Bromophenyl acridine.** ALBERT E. DUNSTAN and JAMES A. STUBBS (*Ber.*, 1906 39, 2402—2404. Compare Dunstan and Oakley, this vol., i, 383).—5-*p*-Bromophenylacridine,  $\text{C}_{13}\text{H}_8\text{N} \cdot \text{C}_6\text{H}_4\text{Br}$ , prepared by heating *p*-bromobenzoic acid with diphenylamine and zinc chloride at 220—230°, forms greenish-yellow, prismatic crystals, melts at 234° and dissolves in benzene, toluene, xylene, or acetic acid, less readily in

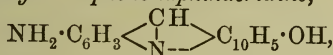
methyl or ethyl alcohol, forming fluorescent solutions. The *chromate*,  $(C_{19}H_{12}NBr)_2, H_2CrO_4$ , the yellow *platinichloride*,  $(C_{19}H_{12}NBr)_2, H_2PtCl_6$ , the *hydrochloride*, which crystallises in green leaflets and melts at  $267^\circ$ , and the *nitrate*, which forms olive-green leaflets and melts at  $172^\circ$ , were prepared. The *methiodide*,  $C_{20}H_{15}NBrI$ , prepared by the action of methyl iodide on the acridine, forms small, dark red crystals and melts and decomposes at  $240^\circ$ .  
G. Y.

**Conversion of *o*-Nitro- and *op*-Dinitro-benzyl Chlorides into Acridine Derivatives.** CARLO BAEZNER and J. GUEORGUIEFF (*Ber.*, 1906, 39, 2438—2447. Compare Baezner, *Abstr.*, 1904, i, 928).—The *acetyl* derivative of 10-amino-1 : 2-phenonaphthacridine,  $C_{19}H_{14}ON_2$ , crystallises in yellow needles, melts at  $267^\circ$ , and dissolves in alcohol, forming an orange-yellow solution with violet fluorescence; the *hydrochloride* is yellow; the *platinichloride*,  $(C_{17}H_{12}N_2)_2, H_2PtCl_6$ , forms reddish-brown crystals; the *zincichloride*,  $(C_{17}H_{12}N_2)_2, H_2ZnCl_4$ , forms slender, red needles; the *chromate* is brownish-red and is insoluble. In solution the salts are yellow and have a green fluorescence.



formed by heating the 9-amino-compound with 10 per cent. sulphuric acid in a sealed tube at  $200\text{--}210^\circ$ , crystallises from nitrobenzene in small, yellow needles, melts at about  $300\text{--}301^\circ$ , is soluble in aqueous alkali hydroxides, and dissolves in concentrated sulphuric acid or alcohol, forming a yellow solution with green fluorescence. The *hydrochloride*,  $C_{17}H_{12}ONCl$ , and the *sodium* salt,  $C_{17}H_{10}ONNa$ , are described. The *acetyl* derivative,  $C_{19}H_{13}O_2N$ , crystallises in white needles, melts at  $160^\circ$ , and has a violet fluorescence in alcoholic solution. The *benzoyl* derivative,  $C_{24}H_{15}O_2N$ , crystallises in small, yellow needles, melts at  $186.5\text{--}187^\circ$ , and dissolves in concentrated sulphuric acid, forming a solution with green, in alcohol forming a solution with violet, fluorescence.

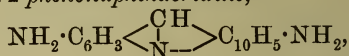
10-Amino-5-hydroxy-1 : 2-phenonaphthacridine,



is formed together with a brownish-red *substance*, which is insoluble in aqueous alkali hydroxides, by the action of stannous chloride and concentrated hydrochloric acid on 2 : 4-dinitrobenzyl chloride and 2 : 7-dihydroxynaphthalene; it crystallises from nitrobenzene in small, orange-yellow needles, melts at  $180^\circ$ , and dissolves in benzene or toluene, forming a yellow solution with bluish-green, in alcohol forming an orange-red solution with green fluorescence, or in mineral acids forming red solutions. The *hydrochloride*,  $C_{17}H_{13}ON_2Cl$ , dyes cotton-wool mordanted with tannin orange-brown. The *acetyl* derivative,  $NHAc \cdot C_{17}H_9N \cdot OH$ , crystallises from nitrobenzene in small, yellow needles, melts at  $283\text{--}285^\circ$ , and dissolves in aqueous alkali hydroxides. The *dibenzoyl* derivative,  $C_{31}H_{20}O_3N_2$ , forms small, bronze-yellow needles, melts at  $212\text{--}215^\circ$ , is insoluble in aqueous alkali hydroxides, and forms solutions in organic solvents with green to violet-blue fluorescence.

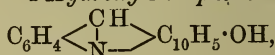
5 : 10-*Dihydroxy*-1 : 2-*phenonaphthacridine*, formed by heating 10-amino-5-hydroxy-1 : 2-phenonaphthacridine with 10 per cent. sulphuric acid in a sealed tube at 190—205°, is soluble only in aqueous alkali hydroxides; the *dibenzoyl* derivative,  $C_{31}H_{19}O_4N$ , melts at 198—201°.

5 : 10-*Diamino*-1 : 2-*phenonaphthacridine*,



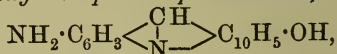
formed together with 10-amino-5-hydroxy-1 : 2-phenonaphthacridine from 2 : 4-dinitrobenzyl chloride and 7-acetylamino-2-naphthol, crystallises in light brown needles, melts at 180°, forms fluorescent solutions, and dyes cotton-wool mordanted with tannin brownish-red.

[With A. GARDIOL.]—4-*Hydroxy*-1 : 2-*phenonaphthacridine*,



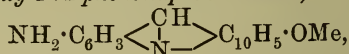
formed from *o*-nitrobenzyl chloride and 2 : 6-dihydroxynaphthalene, melts at 212°, is readily soluble in nitrobenzene, glacial acetic acid, or, forming a yellow solution, in dilute sodium hydroxide. The *hydrochloride*,  $C_{17}H_{12}ONCl$ , was analysed.

10-*Amino*-4-*hydroxy*-1 : 2-*phenonaphthacridine*,



formed from 2 : 4-dinitrobenzyl chloride and 2 : 6-dihydroxynaphthalene, crystallises from nitrobenzene in microscopic, yellowish-brown needles and melts at 218—220°. The *hydrochloride*,  $C_{17}H_{12}ON_2 \cdot HCl$ , melts at 168°. The *acetyl* derivative melts at 263°.

10-*Amino*-1-*methoxy*-1 : 2-*phenonaphthacridine*,



is formed from 2 : 4-dinitrobenzyl chloride and 2-*hydroxy*-3-*methoxy*-*naphthalene*, which is prepared by the action of methyl sulphate on 2 : 3-dihydroxynaphthalene, crystallises in white needles, melts at 65°, and boils at about 285°. The condensation product is isolated as the *acetyl* derivative,  $C_{20}H_{16}O_2N_2$ , which melts at 187°, and on hydrolysis with concentrated hydrochloric acid yields the free *base*. This melts at 137°, gives an orange-brown coloration and green fluorescence with concentrated sulphuric acid, dissolves in ether or hot alcohol, forming a solution with green fluorescence, and yields a *hydrochloride* melting at 212°.

G. Y.

**Existence of isoPyrophthalone.** ALEXANDER EIBNER and M. LÖBERING (*Ber.*, 1906, 39, 2447—2450. Compare *Abstr.*, 1903, i, 644; 1904, i, 921; von Huber, *Abstr.*, 1903, i, 576).—Pyrophthalone, obtained from phthalic anhydride and  $\alpha$ -picoline at 200°, melts when pure at 287°; the *sodium* derivative,  $C_{14}H_8O_2NNa$ , is not decomposed by water and separates from a concentrated aqueous solution in a felted mass of red needles. The *bromotribromide*,  $C_{14}H_8O_2NBr_4$ , forms thick, orange-yellow prisms, and is converted by alcohol, water, and ammonia at the ordinary temperature into *monobromopyrophthalone*,  $C_{14}H_8O_2NBr$ , which, obtained also by brominating pyrophthalone in glacial acetic acid, or the sodium derivative, crystallises

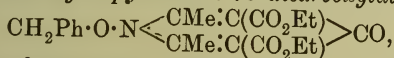


in colourless leaflets, melts at  $157^{\circ}$ , and is changed into pyrophthalone by prolonged boiling with alcohol and water or ammonia. *Anilpyrophthalone*,  $C_{20}H_{14}ON_3$ , prepared in benzene solution with aluminium chloride as condensing agent, separates from alcohol in felted, red needles, melts at  $185^{\circ}$ , and is decomposed by hydrochloric acid; with phenylhydrazine it yields *pyrophthalone phenylhydrazone*,  $C_{20}H_{15}ON_3$ , which forms reddish-brown needles and melts at  $215^{\circ}$ .

Von Huber's "*isopyrophthalone*," obtained from phthalyl chloride and  $\alpha$ -picoline and melting at  $280^{\circ}$ , yields a monobromide and an anil identical with the preceding compounds, and is therefore impure pyrophthalone. From phthalyl chloride and  $\alpha$ -picoline in benzene solution the authors have obtained pyrophthalone in the pure state, melting at  $287^{\circ}$ . C. S.

**Action of Hydroxylamine on Ethyl Dimethylpyrnedicarboxylate.** F. CARLO PALAZZO (*Gazzetta*, 1906, 36, i, 596—611. Compare Abstr., 1904, i, 762).—The author shows that the constitution proposed by him (*loc. cit.*) for the compound  $C_7H_9O_4N$ , obtained by the action of hydroxylamine on ethyl dimethylpyrnedicarboxylate, is erroneous, the true constitution,  $O \begin{array}{c} \text{N} \\ \diagup \\ \text{C}(\text{OH}) \end{array} \begin{array}{c} \text{CMe} \\ \diagdown \\ \text{C} \end{array} \text{CO}_2\text{Et}$ , being that of *ethyl 5-hydroxy-3-methylisooxazole-4-carboxylate*.

The action of benzylhydroxylamine on ethyl dimethylpyrnedicarboxylate differs from that of hydroxylamine, and gives rise to *ethyl 1-benzylloxy-2:6-dimethyl-4-pyridone-3:5-dicarboxylate*,

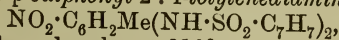


which crystallises from ethyl acetate in white, feathery needles and melts at  $138^{\circ}$ . On boiling with a dilute mineral acid, this compound is transformed into *1-hydroxy-2:6-dimethyl-4-pyridone-3:5-dicarboxylic acid*, which crystallises from alcohol in slender, white needles melting and decomposing at  $245^{\circ}$ , and gives an intense, blood-red coloration with ferric chloride. T. H. P.

**Nitration of *m*-Diarylsulphondiamides.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 166600).—The *m*-diarylsulphondiamides are readily nitrated with warm dilute nitric acid, the reaction being accelerated either by efficient stirring or by the addition of an inert solvent for the diamide. The *m*-diarylsulphondiamides are prepared from the *m*-diamines by treating these bases (1 mol.) with the arylsulphonic chloride (2 mols.) in the presence of aqueous sodium carbonate.

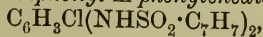
*s*-Ditoluene-*p*-sulphonyl-*m*-phenylenediamine, which is obtained in white crystals melting at  $172^{\circ}$ , yields 4-nitro-*s*-ditoluene-*p*-sulphonyl-*m*-phenylenediamine, a brownish-yellow, crystalline substance melting at  $169^{\circ}$ .

6-Nitro-*s*-ditoluene-*p*-sulphonyl-2:4-tolylenediamine,



forms yellow crystals and melts at  $210^{\circ}$ .

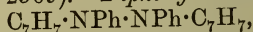
4-Chloro-*s*-ditoluene-*p*-sulphonyl-*m*-phenylenediamine,



separates in white prisms melting at  $215^{\circ}$ , and yields 4-chloro-6-nitro-s-ditoluene-p-sulphonyl-m-phenylenediamine, which crystallises in yellow prisms and melts at  $196^{\circ}$ .

s-Dibenzenesulphonyl-2 : 4-tolylenediamine crystallises in white needles melting at  $191^{\circ}$ ; its nitro-derivative is obtained in yellow prisms and melts at  $185^{\circ}$ .  
G. T. M.

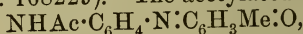
**A New Method of Preparation and the Properties of Quaternary Hydrazines.** HARTWIG FRANZEN and F. ZIMMERMANN (*Ber.*, 1906, 39, 2566—2569).—Diphenyldibenzylhydrazine,



obtained by boiling diphenyldibenzyltetrazone with xylene, is a faintly yellow oil which boils at  $181-181.5^{\circ}$  under 19 mm. pressure, forms an unstable hydrochloride,  $C_{26}H_{24}N_2 \cdot 2HCl$ , which crystallises in white needles and melts at  $215.5^{\circ}$ , and is decomposed by boiling 2*N*-sulphuric acid into aniline, benzyaniline, and benzaldehyde.

Diphenyldimethyltetrazone is decomposed in boiling xylene, forming ammonia and phenyl isocyanide.  
C. S.

**Acetylated Indophenols.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 168229).—The acetylated indophenol,



obtained by oxidising an alkaline solution of *p*-aminoacetanilide and *o*-cresol with sodium hypochlorite, is a reddish-brown powder, very soluble in alcohol, which crystallises from hot water in brick-red needles. A similar compound is obtained when phenol is substituted for *o*-cresol. When these substances are warmed with aqueous sodium sulphide they are simultaneously hydrolysed and reduced to leuco-derivatives.  
G. T. M.

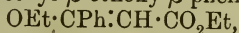
**Action of Sulphuryl Chloride on Pyrazole.** GIROLAMO MAZZARA and ALESSANDRO BORGIO (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 704—710).—The action of sulphuryl chloride (1 mol.) on an ethereal solution of pyrazole maintained at  $0^{\circ}$  yields 4-chloropyrazole, which crystallises in the rhombic system [C. VIOLA :  $a : b : c = 0.8026 : 1 : 0.8284$ ] and melts at  $77^{\circ}$  ( $69-71^{\circ}$ , Knorr, *Abstr.*, 1895, i, 396).

4-Chloro-1-methylpyrazole,  $C_3H_2N_2ClMe$ , prepared by treating a methyl-alcoholic solution of 4-chloropyrazole with methyl-alcoholic potassium hydroxide and methyl iodide, is a yellow, oily liquid, which boils at  $167^{\circ}$  under 756 mm. pressure, has a penetrating and irritating odour, and is turned red by the action of light.  
T. H. P.

**Researches on Pyrazolones.** New Methods of Synthesis of Pyrazolones. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 142, 1534—1537).—Ethyl amylpropionate,  $C_5H_{11} \cdot C : C \cdot CO_2Et$ , and ethyl hexoacetate,  $C_5H_{11} \cdot CO \cdot CH_2 \cdot CO_2Et$ , react with phenylhydrazine to form the same phenylamylpyrazolone melting at  $96^{\circ}$ ; similarly, the same phenylhexylpyrazolone melting at  $84-85^{\circ}$  is obtained by the action of phenylhydrazine on ethyl hexylpropionate,  $C_6H_{13} \cdot C : C \cdot CO_2Et$ , or on methylheptoacetate,  $C_6H_{13} \cdot CO \cdot CH_2 \cdot CO_2Et$  (compare Rothenburg, *Abstr.*, 1893, i, 611); the phenylamylpyraz-

olone and phenylhexylpyrazolone thus prepared are isomeric with the compounds obtained by the action of phenylhydrazine on ethyl  $\beta$ -ethoxy- $\beta$ -amylacrylate or ethyl  $\beta$ -ethoxy- $\beta$ -hexylacrylate, which melt at  $280^\circ$  and  $270^\circ$  respectively.

Hydrazine hydrate condenses with phenylpropiolamide,  
 $\text{CPh:C}\cdot\text{CO}\cdot\text{NH}_2$   
 (this vol., i, 148), or with ethyl  $\beta$ -ethoxy- $\beta$ -phenylacrylate,



to yield a phenylpyrazolone melting at  $237^\circ$ , which is identical with the compound prepared similarly from ethyl phenylpropiolate or ethyl benzoylacetate (Rothenburg, *loc. cit.*).

Phenylhydrazine reacts with ethyl  $\beta$ -ethoxy- $\beta$ -phenylacrylate to form a diphenylpyrazolone which melts at  $256^\circ$  and is identical with the compound prepared by Knorr by the action of heat on phenylcinnamoylhydrazine (Abstr., 1887, 665), and isomeric with the diphenylpyrazolone melting at  $136^\circ$ , which is formed by the action of phenylhydrazine on ethyl phenylpropiolate or ethyl benzoylacetate; it is probable that the isomeride melting at  $256^\circ$  is 1:5-diphenyl-3-

pyrazolone,  $\text{CO}\begin{smallmatrix} \text{NH}\cdot\text{NPh} \\ \text{CH:CPh} \end{smallmatrix}$ , formed by the elimination of  $\text{C}_2\text{H}_5\cdot\text{OH}$

from the intermediate compound,  $\text{OEt}\cdot\text{CPh:CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ , and that the isomeride melting at  $136^\circ$  is 2:5-diphenyl-3-pyrazolone,

$\text{CO}\begin{smallmatrix} \text{NPh}\cdot\text{NH} \\ \text{CH}=\text{CPh} \end{smallmatrix}$ , similarly formed from the intermediate compound,

$\text{NHPh}\cdot\text{NH}\cdot\text{CPh:CH}\cdot\text{CO}_2\text{Et}$  (compare Buchner, Abstr., 1890, 156, and Rothenburg, *loc. cit.*).

M. A. W.

**Preparation of Cyclic Carbamide Derivatives (Pyrimidines).** EMANUEL MERCK (D.R.-P. 170555, 170657).—4-Amino-2:6-dihydroxypyrimidine is obtained by adding ethyl cyanoacetate to a mixture of acetylcarbamide and sodamide in xylene; the mixture, which is cooled during the addition of the ester, is afterwards heated at  $150^\circ$  for five to six hours, when the product is treated with water and the pyrimidine precipitated with acetic acid.

4-Amino-2:6-dihydroxy-3-methylpyrimidine is prepared similarly from acetylmethylcarbamide, sodamide, and ethyl cyanoacetate; the final aqueous extract contains its sodium salt, and the free pyrimidine is precipitated with acetic acid.

The foregoing pyrimidine can also be prepared from the same reagents, using, however, instead of sodamide, a solution of sodium ethoxide in absolute alcohol.

G. T. M.

**Preparation of 5:5-Dialkylbarbituric Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 163136. Compare this vol., i, 538).—Dialkylmalonodiamides and alkyl carbonates condense in presence of alkali ethoxides to form 5:5-dialkylbarbituric acids; as  $\text{CEt}_2(\text{CO}\cdot\text{NH}_2)_2 + \text{CO}(\text{OEt})_2 = 2\text{EtOH} + \text{CEt}_2\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}\text{CO}$ . Alkali hydroxides cannot be substituted for ethoxides, as decomposition then takes place.

C. H. D.



**Preparation of 5:5-Diethylbarbituric Acid.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 167332).—Although at 100° diethylmalonamide and carbonyl chloride interact to form large quantities of diethylmalononitrile, whilst the carbamide is not produced, yet when the condensation is carried out at 150° less of the nitrile is formed, whilst a 30 to 40 per cent. yield of the carbamide derivative is obtained. The residue when crystallised from water yields pure diethylbarbituric acid melting at 191°. G. T. M.

**Preparation of Dialkylbarbituric Acids and Dialkyloxy-pyrimidine Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 168406, 168407. See preceding abstracts).—The alkyl or aryl carbonates and dialkylmalonamides condense to form substituted barbituric acids when heated in contact with sodium or sodamide. Thus diethylbarbituric acid may be obtained from ethyl carbonate and diethylmalonamide and dipropylbarbituric acid from phenyl carbonate and dipropylmalonamide.

Diethylthiobarbituric acid may be prepared by heating diethylmalonamide, carbon disulphide, and sodium ethoxide in alcoholic solution at 100°. The product is crystallised from water.

Diethylbarbituric and dipropylbarbituric acids are formed when diethylmalonamide and dipropylmalonamide respectively are heated at 100° with carbon oxysulphide and alcoholic sodium ethoxide.

G. T. M.

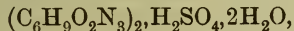
**Pyrimidines. Synthesis of *iso*Barbituric Acid and of 5-Hydroxycytosine.** TREAT B. JOHNSON and ELMER V. MCCOLLUM (*J. Biol. Chem.*, 1906, i, 437—449. Compare Abstr., 1903, i, 526).—A mixture of ethyl formate and ethyl ethylglycollate reacts with sodium suspended in ether, yielding the sodium derivative of *ethyl β-hydroxy-α-ethoxyacrylate*,  $\text{NaO}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{CO}_2\text{Et}$ , which condenses with an aqueous solution of  $\psi$ -ethylthiocarbamide hydrobromide and potassium hydroxide, yielding 6-*oxy-5-ethoxy-2-ethylthiolpyrimidine*,  $\text{SEt}\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{N}-\text{CH} \end{smallmatrix} \text{C}\cdot\text{OEt}$ . This crystallises from alcohol in rhombic prisms, melts at 169°, and is only sparingly soluble in hot water. It is not decomposed when boiled with hydrochloric or hydrobromic acid; with 20 per cent. hydrochloric acid at 150° it yields ethyl chloride, ethyl mercaptan, *isobarbituric acid*, and probably 2:6-dihydroxy-5-ethoxypyrimidine. A good yield of *isobarbituric acid* is obtained when the pyrimidine derivative is hydrolysed with concentrated hydrochloric acid at 150°.

6-*Chloro-5-ethoxy-2-ethylthiolpyrimidine*,  $\text{SEt}\cdot\text{C}\begin{smallmatrix} \text{N}:\text{CCl} \\ \text{N}\cdot\text{CH} \end{smallmatrix} \text{C}\cdot\text{OEt}$ , obtained by the action of phosphorus oxychloride on the corresponding oxypyrimidine, crystallises in colourless prisms, melts at 46°, and distils at 185° under 25 mm. pressure. It forms an additive compound with phosphorus oxychloride, which is decomposed by hot water. Alcoholic ammonia reacts with the chloro-derivative at 150—160°, yielding 6-*amino-5-ethoxy-2-ethylthiolpyrimidine*,  $\text{C}_8\text{H}_{13}\text{ON}_3\text{S}$ , which

crystallises from hot water in rhombic prisms melting at  $105^{\circ}$ . The amino-compound is decomposed by 20 per cent. hydrochloric acid at  $150$ — $160^{\circ}$  into ethyl mercaptan and *isobarbituric acid*, together with the intermediate products 5-ethoxycytosine and 2:6-dioxy-5-ethoxypyrimidine,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{OEt}$ , which crystallises from water in radiating prisms, begins to turn brown at  $220^{\circ}$ , and decomposes at  $260$ — $280^{\circ}$ . 5-Ethoxycytosine,  $\text{CO} \begin{smallmatrix} \text{N} \cdot \text{C}(\text{NH}_2) \\ \text{NH} - \text{CH} \end{smallmatrix} \text{C} \cdot \text{OEt}$ , is readily soluble in warm water, crystallises in slender prisms, and melts at  $300^{\circ}$ . Its *picrate* melts at  $229$ — $231^{\circ}$ .

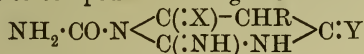
Concentrated hydrochloric acid at  $150^{\circ}$  transforms the aminoethoxyethylthiolpyrimidine into ethyl chloride, ethyl mercaptan, a small amount of *isobarbituric acid*, and 5-hydroxycytosine, the *picrate* of which slowly decomposes above  $240^{\circ}$ .

6-Oxy-5-ethoxy-2-methylthiolpyrimidine crystallises from alcohol in stout prisms and melts at  $190^{\circ}$ . 2-Amino-6-oxy-5-ethoxypyrimidine or 5-ethoxyisocytosine,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{N} - \text{CH} \end{smallmatrix} \text{C} \cdot \text{OEt}$ , obtained by the action of guanidine on ethyl sodio- $\beta$ -hydroxy- $\alpha$ -ethoxyacrylate, is best purified by precipitation with mercuric chloride. The *sulphate*,



decomposes at  $225$ — $226^{\circ}$ . The base crystallises from water in microscopic prisms and melts at  $248^{\circ}$ . J. J. S.

**Preparation of Pyrimidine Derivatives.** EMANUEL MERCK (D.R.-P. 170586).—Guanylcabamide, which may have either of the following formulæ,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2$  or  $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \cdot \text{C}(\text{NH}_2)_2$ , condenses with either ethyl cyanoacetate or ethyl hydrogen malonate to give a mixture of compounds of the pyrimidine series. The first formula would lead to compounds having the formulæ



and  $\text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{N} \begin{smallmatrix} \text{C}(\text{X}) \cdot \text{CHR} \\ \text{CO} - \text{NH} \end{smallmatrix} \text{C} : \text{Y}$ , whilst the second formula for guanylcabamide would give rise to compounds having the following structure:  $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{X}) \\ \text{NH} - \text{C}(\text{Y}) \end{smallmatrix} \text{CHR}$ , where R = hydrogen or an alkyl group, X and Y either oxygen or an imino-group.

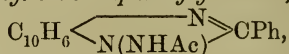
G. T. M.

**Formation of Indazyl Derivatives from *o*-Hydrazobenzoic Acid.** PAUL CARRÉ (*Compt. rend.*, 1906, 143, 54—56).—The compound,  $(\text{C}_{14}\text{H}_8\text{O}_2\text{N}_2)_2$ , obtained by the action of water on benzaldehyde-*o*-azobenzoic acid (compare *Abstr.*, 1905, i, 307) can be prepared more readily by treating *o*-hydrazobenzoic acid with phosphorus pentachloride (compare *Freundler*, this vol., i, 544). The compound yields 3-hydroxy-*o*-indazylbenzoic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OH}) \\ \text{N} \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , on saponification, and is regenerated from this acid by the action of dehydrating agents; it is therefore a *lactone* of 3-hydroxy-*o*-indazylbenzoic acid.

3-Hydroxy-o-indazylbenzoic acid crystallises from alcohol in white plates and melts at 228° with formation of the lactone; the ethyl ester crystallises from alcohol in white needles, melts at 132°, and decomposes at a slightly higher temperature into the lactone and ethyl alcohol. M. A. W.

*N*-Aminoheterocyclic Compounds. I. 1-Amino-2-phenyl-2:3-naphthaglyoxaline. HARTWIG FRANZEN (*J. pr. Chem.*, 1906, [ii], 73, 545—569. Compare Abstr., 1905, i, 244, 830).—If 1:3-dibenzylideneamino-2-phenyldihydro-2:3-naphthaglyoxaline is boiled with glacial acetic acid and a small amount of concentrated hydrochloric acid, and the cooled liquid poured into water and distilled in a current of steam, ammonium chloride and 1-benzylideneamino-2-phenyl-2:3-naphthaglyoxaline are formed; if the distillation is continued, the latter substance is further hydrolysed to benzaldehyde and 1-amino-2-phenyl-2:3-naphthaglyoxaline,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{N}(\text{NH}_2) \end{smallmatrix} \text{CPh}$ . This crystallises from alcohol in small, slightly brown leaflets, melts and decomposes at 264°, dissolves readily in boiling acetone, and is a mono-acid base. Although containing the group  $\text{:N}\cdot\text{NH}_2$ , the properties of the base are entirely different from those of the *as.-sec.-hydrazines*. It reacts only slowly with aromatic aldehydes or phenylthiocarbimide, is not reduced by zinc dust and glacial acetic acid or oxidised when boiled with mercuric oxide and alcohol, does not react with acetone, acetophenone, aliphatic aldehydes, cyanic acid, or sodium and hydrochloric acid, and yields 2-phenyl-2:3-naphthaglyoxaline when boiled with amyl nitrite and concentrated hydrochloric acid in alcoholic solution. The hydrochloride,  $C_{10}H_6 \begin{smallmatrix} \text{N}(\text{HCl}) \\ \text{N}(\text{NH}_2) \end{smallmatrix} \text{CPh}$ , crystallises in slightly yellow needles, melts at 245°, and is decomposed by water; the sulphate,  $(C_{17}H_{13}N_3)_2, H_2SO_4$ , forms matted, yellow needles and melts at 240°; the nitrate,  $C_{17}H_{14}O_3N_4$ , crystallises in yellow needles and melts and decomposes at 176°; the picrate,  $C_{17}H_{13}N_3, C_6H_3O_7N_3$ , forms small, yellow needles and melts and decomposes at 205—206°; the platinichloride,  $(C_{17}H_{13}N_3)_2, H_2PtCl_6$ , is obtained as a yellow precipitate.

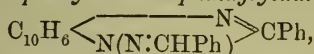
1-Acetyl-amino-2-phenyl-2:3-naphthaglyoxaline,



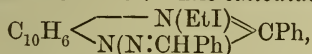
formed by boiling the base with acetic anhydride, crystallises in stout, colourless prisms and melts at 192°. 1-Phenylthiocarbamido-2-phenyl-2:3-naphthaglyoxaline,  $C_{11}H_6N_2Ph\cdot NH\cdot CS\cdot NHPh$ , formed by prolonged boiling of the amino-base with phenylthiocarbimide in alcoholic solution, crystallises in slender, yellow needles and is only sparingly soluble in boiling alcohol. The ethiodide,  $C_{10}H_6 \begin{smallmatrix} \text{N}(\text{EtI}) \\ \text{N}(\text{NH}_2) \end{smallmatrix} \text{CPh}$ , prepared by boiling the base with ethyl iodide in alcoholic solution in a reflux apparatus, crystallises in rosettes of slender, yellow needles, melts and blackens at 195—196°, and when heated with dilute hydrochloric acid is decomposed, forming 1-amino-2-phenyl-2:3-naphthaglyoxaline hydrochloride.



## 1-Benzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline,

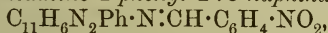


formed in the first stage of the hydrolysis of 1 : 3-dibenzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline or by prolonged boiling of the 1-amino-base with benzaldehyde in alcoholic solution, crystallises in slender, yellow or yellowish-brown needles and melts at 169°; the *hydrochloride*,  $\text{C}_{24}\text{H}_{18}\text{N}_3\text{Cl}$ , forms light yellow, slender needles and sinters at 210°, but does not melt at 285°; the *sulphate*,  $\text{C}_{48}\text{H}_{36}\text{O}_4\text{N}_6\text{S}$ , forms slender, yellow needles and sinters at 235°, but does not melt at 285°; the *picrate*,  $\text{C}_{30}\text{H}_{20}\text{O}_7\text{N}_6$ , forms slender, yellow needles and melts and decomposes at 248—249°. The *ethiodide*,



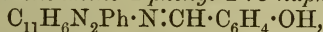
crystallises in slender, yellow needles and melts and decomposes at 218°.

## 1-o-Nitrobenzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline,



crystallises in golden-brown needles and melts at 217—218°.

## 1-o-Hydroxybenzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline,



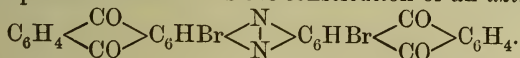
crystallises in slightly yellow needles and melts and blackens at 284°.

2-Phenyl-2 : 3-naphthaglyoxaline,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{CPh}$ , is prepared

together with benzylamine and dibenzylamine by reducing the 1-benzylideneamino-compound with zinc dust and glacial acetic acid; it crystallises in small needles or leaflets and melts at 210—211°, or, after resolidification, at 192°. The *hydrochloride*,  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{Cl}$ , forms a yellow, crystalline mass and commences to sinter at 170°, but does not melt at 285°; the *sulphate*,  $(\text{C}_{17}\text{H}_{12}\text{N}_2)_2\cdot\text{H}_2\text{SO}_4$ , is obtained as a yellow, flocculent precipitate.

G. Y.

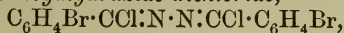
**Conversion of Anthracene Derivatives into Azines and Dihydroazines.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co (D.R.-P. 167255).—When 1 : 3-dibromo-2-aminoanthraquinone is heated at 150° with nitrobenzene, copper chloride, and fused sodium acetate, a compound is produced which has the constitution of an *azine*,



At 180° an appreciable amount of the dihydroazine is also formed. The azine is obtained in the form of greenish-yellow, very sparingly soluble crystals which dissolve in fuming sulphuric acid and yield a colouring matter on boiling with aniline or quinoline (compare Abstr., 1905, i, 797).

G. T. M.

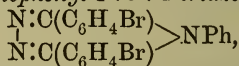
**Conversion of Hydrazine Derivatives into Heterocyclic Compounds.** XXI. Diacylhydrazide Dichlorides of Substituted Benzoic Acids and their Reaction Products. ROBERT STOLLÉ and ANTON WEINDEL (*J. pr. Chem.*, 1906, [ii], 74, 1—12. Compare Stollé, this vol., i, 453; Stollé and Thoma, *ibid.*, 461).—Di-p-bromobenzoylhydrazide dichloride,



formed together with 2:5-di-*p*-bromophenyl-1:3:4-oxadiazole by heating di-*p*-bromobenzoylhydrazide with phosphorus pentachloride at 120°, separates from ether in stout, transparent crystals, from alcohol in transparent, slightly yellow leaflets, melts at 145°, dissolves in concentrated sulphuric acid, forming a golden-yellow solution, and yields 2:5-di-*p*-bromophenyl-1:3:4-oxadiazole when heated with alcoholic silver nitrate, or more slowly when boiled with water.

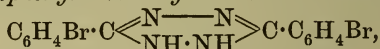
2:5-Di-*p*-bromophenyl-1:3:4-triazole,  $\begin{array}{c} \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \\ | \\ \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \end{array} > \text{NH}$ , formed by heating the dichloride with alcoholic ammonia in a sealed tube at 150°, crystallises in long needles, melts at 284°, dissolves in aqueous sodium hydroxide, and is reprecipitated by carbon dioxide, and forms a stable white *precipitate* with silver nitrate in alcoholic solution.

1-Phenyl-2:5-di-*p*-bromophenyl-1:3:4-triazole,



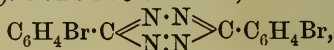
prepared by the action of aniline on the dichloride at 170°, crystallises in matted, slender needles and melts at 261°.

3:6-Di-*p*-bromophenyl-1:2-dihydro-1:2:4:5-tetrazine,



prepared by boiling the dichloride with hydrazine hydrate in ethereal solution, separates from benzene in yellow crystals, melts and decomposes at 235°, forming an intensely red liquid, and is oxidised by silver nitrate in alcoholic solution, metallic silver being precipitated, or more slowly on exposure of the alcoholic solution to air, forming

3:6-di-*p*-bromophenyl-1:2:4:5-tetrazine,

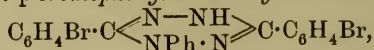


which crystallises from benzene in bluish-red leaflets and does not melt at 280°, but decomposes when more highly heated, yielding a colourless sublimate smelling of benzonitrile.

3:6-Di-*p*-bromophenyl-1:4-dihydro-1:2:4:5-tetrazine hydrochloride,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{NH} \\ \text{NH} \cdot \text{N} \end{array} \text{C} \cdot \text{C}_6\text{H}_4\text{Br}, \text{HCl}$ , formed by the action of hydrogen chloride on the 1:2-dihydropyrazine in alcoholic solution, crystallises in small prisms. The *base*,  $\text{C}_{14}\text{H}_{10}\text{N}_4\text{Br}_2$ , crystallises from alcohol in glistening, white needles, does not melt at 300°, and forms a stable, white *precipitate* with silver nitrate in alcoholic solution.

1:2-Dibenzoyl-3:6-di-*p*-bromophenyl-1:2-dihydro-1:2:4:5-tetrazine,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{C} \begin{array}{c} \text{N} \text{---} \text{N} \\ \text{NBz} \cdot \text{NBz} \end{array} \text{C} \cdot \text{C}_6\text{H}_4\text{Br}$ , prepared by the action of benzoyl chloride on the 1:2-dihydropyrazine in pyridine solution, separates from alcohol as a yellow, crystalline powder and melts at 248°.

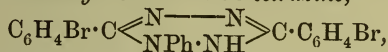
1-Phenyl-3:6-di-*p*-bromophenyl-1:4-dihydro-1:2:4:5-tetrazine,



prepared by heating di-*p*-bromobenzoylhydrazide dichloride with phenylhydrazine in alcoholic solution on the water-bath, forms small,

glistening, white, granular crystals and melts and decomposes at 260°.

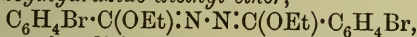
The action of phenylhydrazine on di-*p*-bromobenzoylhydrazide dichloride in pyridine solution leads to the formation of 1-*phenyl*-3:6-di-*p*-bromophenyl-1:2-dihydro-1:2:4:5-tetrazine,



which crystallises from alcohol in yellow needles, melts and decomposes at 167°, and forms a brown *precipitate* with silver nitrate in alcoholic solution.

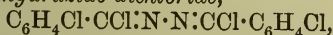
The action of *m*-nitrobenzylidenehydrazide and pyridine on di-*p*-bromobenzoylhydrazide dichloride in boiling benzene solution leads to the formation of 3:6-di-*p*-bromophenyl-1:2:4:5-tetrazine and 2:5-di-*p*-bromophenyl-1:3:4-oxadiazole.

*Di-p-bromobenzoylhydrazide diethyl ether*,



formed by boiling the dichloride with sodium ethoxide in alcoholic solution in a reflux apparatus, crystallises in matted, slender needles, melts at 111°, and is hydrolysed by hydrochloric acid at 150°, forming hydrazine, *p*-bromobenzoic acid, and ethyl chloride. When heated with alcoholic ammonia in a sealed tube at 200°, it forms 2:5-di-*p*-bromophenyl-1:3:4-triazole.

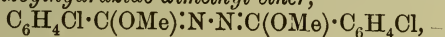
*Di-p-chlorobenzoylhydrazide dichloride*,



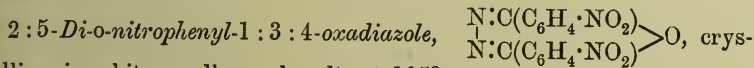
forms large, glistening crystals, melts at 125°, dissolves in ether or hot alcohol, forming green solutions, and yields silver chloride only slowly when boiled with alcoholic silver nitrate.

3:6-Di-*p*-chlorophenyl-1:2-dihydro-1:2:4:5-tetrazine,  $\text{C}_{14}\text{H}_{10}\text{N}_4\text{Cl}_2$ , forms yellow crystals, melts, becoming red, at 215°, and is oxidised to the *tetrazine*, which crystallises in bluish-red leaflets, by alcoholic silver nitrate at the ordinary temperature, by amyl nitrite in hot benzene solution, or more slowly on exposure of the alcoholic solution to air.

*Di-p-chlorobenzoylhydrazide dimethyl ether*,



melts at 162°.



tallises in white needles and melts at 195°.

1-*Phenyl*-2:5-di-*m*-nitrophenyl-1:3:4-triazole,  $\text{C}_{20}\text{H}_{13}\text{O}_4\text{N}_5$ , crystallises in matted, white needles and melts at 215°.

The action of phosphorus pentachloride on benzoylhydrazide leads to the formation of 2:5-diphenyl-1:3:4-triazole and a *compound*,  $\text{NHBz}\cdot\text{NH}\cdot\text{P}(\text{N}\cdot\text{NHBz})_2$ , which crystallises from alcohol and melts at about 220°.

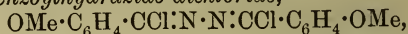
G. Y.

Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXII. Diacylhydrazide Dichlorides of Substituted Benzoic Acids and of  $\alpha$ -Naphthoic Acid. ROBERT STOLLÉ and ADOLF BAMBACH (*J. pr. Chem.*, 1906, [ii], 74, 13—24. Compare Stollé, this vol., i, 453; Stollé and Thoma, *ibid.*, 461).—*Di-p-methoxybenzoylhydrazide*,  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2$ , which forms colourless

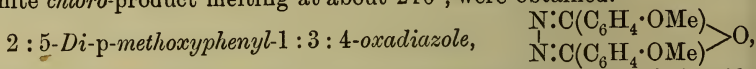


crystals and melts at  $224^{\circ}$ , is prepared together with *p*-methoxybenzoylhydrazide by the action of anisyl chloride on hydrazine sulphate in dilute potassium hydroxide solution. The latter substance is isolated as the *benzylidene* derivative,  $C_{15}H_{14}O_2N_2$ , which crystallises from alcohol in white needles and melts at  $198^{\circ}$ .

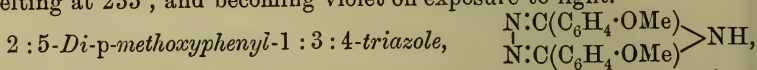
*Di-p-methoxybenzoylhydrazide dichloride*,



formed together with the corresponding oxadiazole, crystallises from ether or alcohol in needles or leaflets, melts at  $130-150^{\circ}$ , gives a golden-yellow coloration with concentrated sulphuric acid, and yields silver chloride when heated with alcoholic silver nitrate. In one preparation a compound containing chlorine and nitrogen, crystallising in green, glistening needles and melting at about  $185^{\circ}$ , and in another a white *chloro*-product melting at about  $210^{\circ}$ , were obtained.

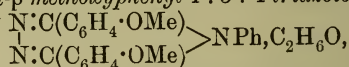


formed by heating di-*p*-methoxybenzoylhydrazide with thionyl chloride in a reflux apparatus or alone at  $260^{\circ}$ , crystallises from alcohol in glistening, white needles, melts at  $164^{\circ}$ , and forms a white, flocculent precipitate,  $C_{16}H_{14}O_3N_2 \cdot AgNO_3$ , with silver nitrate in alcoholic solution, melting at  $233^{\circ}$ , and becoming violet on exposure to light.



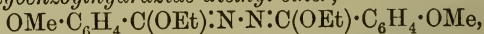
forms white leaflets or rhombic crystals, melts when slowly heated at  $180-182^{\circ}$ , or at  $150^{\circ}$  if suddenly heated, dissolves in hot sodium carbonate solution, and yields a white precipitate with silver nitrate.

*1-Phenyl-2 : 5-di-p-methoxyphenyl-1 : 3 : 4-triazole*,



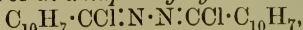
crystallises in white, silky fibres, loses  $C_2H_6O$  at  $100^{\circ}$ , melts at  $250^{\circ}$ , is slightly soluble in acids, but insoluble in aqueous alkali hydroxides, and forms a flocculent precipitate with silver nitrate in alcoholic solution.

*Di-p-methoxybenzoylhydrazide diethyl ether*,

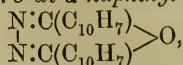


crystallises from alcohol in white needles, melts at  $116-117^{\circ}$ , and is hydrolysed by boiling hydrochloric acid and alcohol.

The action of phosphorus pentachloride on di-*a*-naphthoylhydrazide leads to the formation of *di-a-naphthoylhydrazide dichloride*,



which forms stout crystals, melts at  $104-105^{\circ}$ , gives an orange coloration with concentrated sulphuric acid, and is converted by silver nitrate in alcoholic solution into *2 : 5-di-a-naphthyl-1 : 3 : 4-oxadiazole*,



which forms a crystalline powder, melts at  $175^{\circ}$ , and shows a violet fluorescence in alcoholic or ethereal solution (compare Ekstrand, Abstr., 1887, 373, 840).

*Di-p-nitrobenzoylhydrazide dichloride*,  $C_{14}H_8O_4N_4Cl_2$ , crystallises from

xylene or acetone in lemon-yellow needles, melts at  $187^{\circ}$ , and reacts with silver nitrate only slowly in boiling alcoholic solution.

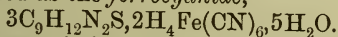
2:5-Di-*p*-nitrophenyl-1:3:4-oxadiazole,  $C_{14}H_8O_5N_4$ , crystallises in glistening, yellowish-brown or rose leaflets, melts at  $302^{\circ}$ , and is only sparingly soluble in hot organic solvents.

When heated with alcoholic ammonia at  $200^{\circ}$ , the dichloride yields 2:5-di-*p*-nitrophenyl-1:3:4-triazole (Pinner, Abstr., 1898, i, 94).

1-Phenyl-2:5-di-*p*-nitrophenyl-1:3:4-triazole,  $C_{20}H_{13}O_4N_5$ , separates from acetone in matted, white needles or from alcohol in small, stout crystals, melts at  $270^{\circ}$ , and forms a gelatinous *additive* compound with silver nitrate.

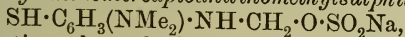
G. Y.

**Action of Formaldehyde on *as*-Dimethyl-*p*-phenylenediaminethiosulphonic Acid and a New Method of preparing Benzothiazoles.** OTTO SCHMIDT (*Ber.*, 1906, 39, 2406—2413. Compare Rügheimer, this vol., i, 418).—Anhydroformaldehyde dimethyl-*p*-phenylenediamine mercaptan [5-dimethylamino-2-methyleneamino-phenyl mercaptan],  $SH \cdot C_6H_3(NMe_2) \cdot N:CH_2$ , is formed by the action of formaldehyde and hydrochloric acid on *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid dissolved in aqueous ammonia; it polymerises rapidly and is isolated as the *ferrocyanide*,



The action of sodium nitrite and hydrochloric acid on the freshly-prepared cooled solution of the mercaptan leads to the formation of 5-dimethylaminobenzothiazole,  $NMe_2 \cdot C_6H_3 < \begin{smallmatrix} N \\ S \end{smallmatrix} > CH$ , together with a small amount of a *substance*, which crystallises in matted, red needles and melts at  $128^{\circ}$ . The *benzothiazole* is formed also by boiling *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid with formic acid; it crystallises in colourless leaflets, melts at  $73$ — $74^{\circ}$ , is a feeble base, and gives a greenish-blue coloration, which becomes sky-blue on addition of water, with ferric chloride.

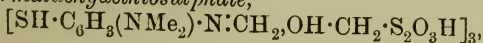
*Sodium p*-dimethylaminomercaptoanilinomethylsulphite,



is formed by heating the anhydro-compound with sodium hydrogen sulphite solution at  $60^{\circ}$ ; it crystallises from concentrated sodium hydroxide solution, and when treated with sodium nitrite in dilute acetic acid solution yields 5-dimethylamino-1:2-dihydrobenzothiazyl hydrogen sulphite,  $NMe_2 \cdot C_6H_3 < \begin{smallmatrix} NH \\ S \end{smallmatrix} > CH \cdot O \cdot SO_2H$ . This forms small, lemon-yellow leaflets or needles, does not melt at  $300^{\circ}$ , dissolves in strong acids or bases, forming coloured salts, and yields 5-dimethylaminobenzothiazole when heated or when boiled with aqueous alkali hydroxides.

G. Y.

**Compounds of Thiosulphuric Acid with Aldehydes.** OTTO SCHMIDT (*Ber.*, 1906, 39, 2413—2419. Compare preceding abstract; Vanino, Abstr., 1902, i, 744).—5-Dimethylamino-2-methyleneamino-phenylthiol formaldehydethiosulphate,



is formed by the action of sodium thiosulphate, formaldehyde, and hydrochloric acid on dimethyl-*p*-phenylenediaminethiosulphonic acid in ammoniacal solution; it crystallises in glistening, white, rhombic leaflets, melts and decomposes at about 122°, dissolves and partially decomposes when boiled with water, and is insoluble in organic solvents. When boiled with aqueous sodium hydroxide it forms sodium thiosulphate, formaldehyde, and the trimeride of the anhydro-mercaptan. In presence of an excess of formaldehyde, sodium thiosulphate is decomposed by hydrochloric acid, forming sulphuric acid, trithioformaldehyde being formed at the same time. If the formaldehyde is not in excess, sulphur and sulphur dioxide are formed. The decomposition of the formaldehydethiosulphate by hydrochloric acid takes place in the same manner.

The formaldehydethiosulphate is converted into 5-dimethylamino-benzothiazole in the same manner as is the free anhydro-compound (preceding abstract). G. Y.

**Action of Carbonyl Chloride on 4-Acetylamino-*m*-phenylenediamine.** LEOPOLD CASSELLA & Co. (D.R.-P. 166680).—When carbonyl chloride is passed into a solution of 4-acetylamino-*m*-phenylenediamine in aqueous sodium carbonate, an insoluble carbamide is precipitated. This *diacetyltetra-aminodiphenylcarbamide* is insoluble in all the ordinary solvents and melts above 300°. When fused with sulphur at 240°, it yields a colouring matter containing sulphur, and soluble in alkali sulphides. G. T. M.

**Colourless Soluble Salts of Rosaniline.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 163104).—Both triaminoditolylphenylcarbinol and triaminotritolylcarbinol dissolve in concentrated hydrochloric acid on a boiling water-bath, and crystals of a colourless salt separate on cooling. The product is washed with hydrochloric acid and dried in a vacuum, or, if necessary, washed with alcohol and ether. These salts dissolve very readily in cold water to form colourless solutions, which become red when heated, owing to dissociation. C. H. D.

**Quinazolines. XV. A 3-Aminoquinazoline and the Corresponding 3:3'-Di-quinazolyl from 6-Nitroacetylanthranil and Hydrazine Hydrate.** MARSTON T. BOGERT and HARVEY A. SEIL (*J. Amer. Chem. Soc.*, 1906, 28, 884—893. Compare Abstr., 1905, i, 945).—When 6-nitroacetylanthranil (1 mol.) is added to hydrazine hydrate (1 mol.) in 33 per cent. aqueous solution, 5-nitro-3-amino-4-

*keto-2-methyldihydroquinazoline*, 
$$\begin{array}{c} \text{CH} \cdot \text{CH} = \text{C} \cdot \text{N} = \text{C}^{\text{Me}} \\ | \qquad \qquad | \\ \text{CH} \cdot \text{C}(\text{NO}_2) : \text{C} \cdot \text{CO} \cdot \text{N} \cdot \text{NH}_2 \end{array}$$
 is obtained;

this crystallises in long, colourless prisms, melts at 152—153° (corr.), and is fairly soluble in water, alcohol, or acetone, slightly so in chloroform or benzene, and nearly insoluble in ether; the *hydrochloride* melts at 253—254° (corr.); the *platinichloride* forms yellow crystals.

The *diacetyl* derivative, 
$$\begin{array}{c} \text{CH} \cdot \text{CH} = \text{C} \cdot \text{N} = \text{C}^{\text{Me}} \\ | \qquad \qquad | \\ \text{CH} \cdot \text{C}(\text{NO}_2) : \text{C} \cdot \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{Ac}_2 \end{array}$$
 crystallises from

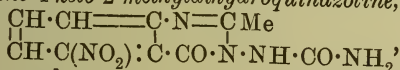


warm alcohol in long, white, slender needles, melts at  $233^{\circ}$  (corr.), and yields a bromo-derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{Ac}_2 \end{smallmatrix}$ , which separates from dilute alcohol in small, yellow crystals, softens at  $105^{\circ}$ , and melts at  $110^{\circ}$  (corr.).

The aminoquinazoline yields an isonitrile-like odour with chloroform and potassium hydroxide, and undergoes condensation with benzaldehyde. It dissolves in warm aqueous potassium hydroxide to a purple-red solution, which, on neutralisation with acetic acid, deposits brown crystals of a nitrogenous substance, melting at  $259\text{--}260^{\circ}$  (uncorr.).

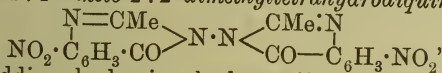
By the action of phenylhydrazine on the aminoquinazoline, 5-nitro-3-phenylhydrazino-4-keto-2-methyldihydroquinazoline phenylhydrazone,  $\text{CH} \cdot \text{CH} = \text{C} \cdot \text{N} = \text{CMe}$   
 $\text{CH} \cdot \text{C}(\text{NO}_2) : \text{C} \cdot \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{N} \cdot \text{NH} \cdot \text{NHPh}$ , is produced, which crystallises in large, white, lustrous plates and melts at  $124\text{--}125^{\circ}$  (corr.).

The aminoquinazoline does not react with potassium cyanate. 5-Nitro-3-carbamino-4-keto-2-methyldihydroquinazoline,



prepared by the condensation of 6-nitroacetylanthranil with semicarbazide, melts at  $263\text{--}264^{\circ}$  (uncorr.). The corresponding 7-nitro-compound, obtained from 4-nitroacetylanthranil and semicarbazide, forms masses of white, silky needles and melts at  $266^{\circ}$  (corr.); its aqueous solution gives a flocculent precipitate on the addition of bromine water; its diacetyl derivative melts at  $229\text{--}230^{\circ}$  (corr.).

5:5'-Dinitro-4:4'-diketo-2:2'-dimethyltetrahydrodiquinazolyl,

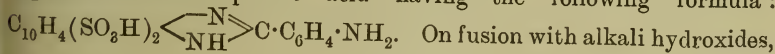


obtained by adding hydrazine hydrate (1 mol.) to finely-powdered 6-nitroacetylanthranil (2 mols.) so that the latter is always in excess, separates from a mixture of alcohol and acetone in small, granular crystals, melts at  $306^{\circ}$ , is not affected by acids or alkalis, and does not yield a bromo-derivative. The diquinazolyl can also be obtained, but only in very small yield, by condensing the aminoquinazoline with another molecule of 6-nitroacetylanthranil. The substance unites with 1 mol. of acetic anhydride to form an additive compound which crystallises in cubes, softens at  $223^{\circ}$ , and melts at  $228^{\circ}$  (corr.).

E. G.

### Aminohydroxy-derivatives of the Phenyl-naphthiminazoles.

AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 167139).—When a nitrobenzaldehyde reacts with one of the naphthylene-o-diaminedisulphonic acids in the presence of acids, a nitrobenzylidene derivative is produced, which, when reduced, yields an aminophenyl-naphthiminazoledisulphonic acid having the following formula:



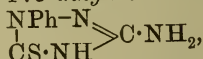
the acid loses one of its sulpho-groups, and an aminohydroxy-derivative is produced.

*3'-Aminophenyl-1:2-naphthiminazole-5:7-disulphonic acid*, obtained by condensing *m*-nitrobenzaldehyde and naphthylene-1:2-diamine-5:7-disulphonic acid in sodium hydrogen sulphite solution and reducing the intermediate nitro-compound with iron filings and dilute hydrochloric acid, is a yellow powder moderately soluble in water and dissolving readily in aqueous alkalis; when fused with alkali hydroxides, it yields *3'-aminophenyl-5-hydroxy-1:2-naphthiminazole-7-sulphonic acid*, an almost colourless powder, which is sparingly soluble in water, but readily dissolved by aqueous alkalis.

Similar compounds are obtained from naphthylene-2:3-diamine-5:7-disulphonic acid, and the *m*-nitrobenzaldehyde may be replaced by other aldehydes, such as *p*-nitrobenzaldehyde and 3-nitro-4-dimethylaminobenzaldehyde-6-sulphonic acid. G. T. M.

**Action of Phenylhydrazine on Unsaturated Disulphides. Synthesis of Triazoles.** EMIL FROMM and KURT SCHNEIDER (*Annalen*, 1906, 348, 174—198).—The action of phenylhydrazine on perthiocyanic acid leads to the formation of phenyldithiourazole (3:5-dithiol-1-phenyl-1:2:4-triazole), 3-amino-5-thio-1-phenyl-4:5-dihydro-(or 5-amino-1-phenyl-3-thio-2:3-dihydro-)-1:2:4-triazole, and anilthiouret.

*3-Amino-5-thio-1-phenyl-4:5-dihydro-1:2:4-triazole*,



crystallises from alcohol in slender, yellow needles, melts at 134.5°, is soluble in mineral acids or dilute alkali hydroxides or ammonia, and reacts with sodium hydroxide and benzyl chloride in alcohol, forming *3-amino-5-thiobenzyl-1-phenyl-1:2:4-triazole*,  $\text{NH}_2\cdot\text{C}_2\text{N}_3\text{Ph}\cdot\text{SC}_6\text{H}_5$ , which crystallises in small needles, melts at 116.5°, is stable towards concentrated hydrochloric acid or fused potassium hydroxide, is oxidised by iodine, and evolves nitrogen with nitrous acid, but does not react with hydrogen sulphide in alcoholic ammoniacal solution. The *diacetyl* derivative,  $\text{C}_{19}\text{H}_{18}\text{ON}_4\text{S}$ , forms a white powder, melts at 122°, and is insoluble in acids or aqueous alkalis.

*3:5-Dithiol-1-phenyl-1:2:4-triazole*,  $\begin{array}{c} \text{NPh}\cdot\text{N} \\ | \\ \text{C}(\text{SH})\cdot\text{N} \end{array} \gg \text{C}\cdot\text{SH}$ , crystallises

from glacial acetic acid in yellow needles, melts at 193°, is readily soluble in hot water or dilute alkali hydroxides or carbonates, has a strong acid reaction, gives precipitates with the salts of the heavy metals, and is stable towards boiling hydrochloric acid or lead oxide and sodium carbonate. The *acetyl* derivative crystallises in yellow needles and melts at 284—285°; the *dibenzyl ether*,  $\text{C}_{22}\text{H}_{19}\text{N}_3\text{S}_2$ , crystallises in stellate aggregates of needles and melts at 69.5°. When oxidised with iodine in alcoholic solution, the dithioltriazole yields the *product*,  $\text{C}_{16}\text{H}_{10}\text{N}_6\text{S}_4$ , which crystallises from glacial acetic acid and melts at 181°.

*Anilthiouret*,  $\text{NPh}\cdot\text{N}\cdot\text{C} \begin{array}{c} \text{S}\cdot\text{S} \\ \text{NH} \end{array} \gg \text{C}\cdot\text{NH}$ , crystallises from dilute hydrochloric acid as a yellow powder, melts at 224—227°, loses

hydrogen sulphide when boiled with lead oxide and aqueous sodium carbonate, and when treated with benzyl chloride and sodium hydroxide is converted into 5-amino-3-thiobenzyl-1-phenyl-1:2:4-triazole,  $\text{NH}_2 \cdot \text{C}_2\text{N}_3\text{Ph} \cdot \text{S} \cdot \text{CH}_2\text{Ph}$ , which crystallises in thin, glistening leaflets, melts at  $137^\circ$ , and forms a monoacetyl derivative,  $\text{C}_{15}\text{H}_{13}\text{N}_4\text{S} \cdot \text{Ac}$ ; when condensed with acetone, anilthiouret yields the product,  $\text{C}_8\text{H}_8\text{N}_4\text{S}_2$ , which crystallises from alcohol and melts at  $223^\circ$ .

5-Amino-3-thiol- or 3-amino-5-thiol-1-phenyl-2-methyl-2:3-dihydro-1:2:4-triazole,  $\text{C}_9\text{H}_{10}\text{N}_4\text{S}$ , formed by the action of *s*-phenylmethylhydrazine on perthiocyanic acid, crystallises in matted, white needles and melts at  $213^\circ$ .

G. Y.

New Compound obtained by the Action of Iodine on Benzaldehyde Phenylhydrazone in Pyridine Solution. GIOVANNI ORTOLEVA (*Gazzetta*, 1906, 36, i, 473—476. Compare Abstr., 1904, i, 99).—The compound melting at  $265$ — $267^\circ$ , to which the author previously ascribed the formula  $\text{C}_{18}\text{H}_{13}\text{N}_3\text{I}$ , is now shown to have the formula  $\text{C}_{18}\text{H}_{14}\text{N}_3\text{I}$ , and to be the hydriodide of a base,  $\text{C}_{18}\text{H}_{13}\text{N}_3$ , having the constitution

$$\begin{array}{c} \text{CH} \cdot \text{CH} : \text{C} \cdot \text{CPh} \\ | \qquad | \\ \text{CH} - \text{N} : \text{C} \cdot \text{NPh} \end{array} \gg \text{N}.$$

When treated with potassium permanganate, this compound gives a good yield of a new base,  $\begin{array}{c} \text{CH} \cdot \text{CH} : \text{C} \cdot \text{CPh} \\ | \qquad | \\ \text{CH} - \text{N} : \text{C} \cdot \text{NH} \end{array} \gg \text{N}$ , which crystallises from light petroleum in small, mammillary masses melting at  $75$ — $78^\circ$  and is soluble in most organic solvents. This base yields a picrate and hydrochloride, and gives a white precipitate with silver nitrate or mercuric chloride. The *platinichloride* is red, and is decomposed by boiling water, giving the free base; when heated at  $180$ — $200^\circ$ , it loses  $4\text{HCl}$  and is transformed into the *platinosochloride*,  $(\text{C}_{12}\text{H}_7\text{N}_3)_2\text{PtCl}_4$ , which is obtained as a yellow powder. T. H. P.

Preparation of Substituted Di-iminobarbituric Acids. EMANUEL MERCK (D.R.-P. 166448).—Malononitrile and its *C*-alkyl derivatives condense with carbamide and its homologues in the presence of the alkali metals or their amides or alkoxides to yield substituted di-iminobarbituric acids, which are readily converted into the corresponding barbituric acids; these products are of importance in therapeutics.

4:6-Di-imino-2-oxy-5-diethylpyrimidine was thus obtained from diethylmalononitrile, carbamide, and sodium ethoxide at  $100^\circ$ ; it separates in crystalline aggregates and melts at  $277^\circ$  (corr.); it forms salts with the mineral acids, and is soluble in aqueous alkali hydroxides, but not in ammonia.

G. T. M.

Soluble Double Salts of 1:3-Dimethylxanthine and 1:3:7-Trimethylxanthine with Barium Salicylate. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 168293).—When 1 mol. of barium salicylate and 2 mols. of 1:3-dimethylxanthine (theophylline) are mixed in warm water and the solution concentrated under diminished



pressure, a soluble double salt is produced, which has the composition  $\text{Ba}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot 2\text{C}_7\text{H}_8\text{O}_2\text{N}_4$ . A similar double salt,  $\text{Ba}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ , is obtained from 1 : 3 : 7-trimethylxanthine.

G. T. M.

**Soluble Double Salts of 3:7-Dimethyl-1-ethylxanthine.** J. D. RIEDEL (D.R.-P. 170302).—3:7-Dimethyl-1-ethylxanthine in aqueous solution combines with sodium benzoate or salicylate, and with lithium benzoate or salicylate to form soluble double salts, which are obtained either on evaporation or on adding alcohol or acetone.

G. T. M.

[Colouring Matters of the Cyanine Series.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 167770).—2:6-Dimethylquinoline-*p*-methoxyquinolinecyanine ethiodide is produced by heating 2:6-dimethylquinoline ethiodide and *p*-methoxyquinoline ethiodide with alcoholic potash; it is precipitated by ether and recrystallised from alcohol, when it separates in lustrous, brown leaflets.

6-Methoxy-2-methylquinoline-6-methylquinolinecyanine methiodide is similarly obtained from the methiodides of 6-methoxy-2-methylquinoline and 6-methylquinoline by the action of potassium hydroxide in methyl-alcoholic solution; it separates in long, green needles. Both these cyanine colouring matters dissolve in alcohol to reddish-violet solutions.

G. T. M.

**Azoxy-compounds.** ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 480—482).—Treatment of a mixture of aniline and nitrobenzene with sodium yields a salt which ignites spontaneously in the air, the sodium content of which points to the formula  $\text{NPhNa} \cdot \text{NPhO} \cdot \text{ONa}$ ; the salt is readily hydrolysed by water, yielding an appreciable proportion of azoxybenzene. Similarly, the condensation of  $\alpha$ -naphthylamine with  $\alpha$ -nitronaphthalene gives a compound from which a good yield of  $\alpha$ -azoxynaphthalene is obtainable.

The interaction either of aniline and  $\alpha$ -nitronaphthalene or of nitrobenzene and  $\alpha$ -naphthylamine in presence of sodium yields two isomeric compounds, probably represented by the formulæ  $\text{NPh} \cdot \text{NO} \cdot \text{C}_{10}\text{H}_7$  and  $\text{NOPh} \cdot \text{N} \cdot \text{C}_{10}\text{H}_7$ .

The condensation of the amines with nitro-derivatives in presence of sodium is hence general, the most important cases yet met with being represented by the following equations:

- (1)  $\text{OH} \cdot \text{NH}_2 + \text{NO}_2 \cdot \text{C}_6\text{H}_5 = \text{HO} \cdot \text{N}_2\text{O} \cdot \text{C}_6\text{H}_5 + \text{H}_2\text{O}.$
- (2)  $\text{OH} \cdot \text{NH}_2 + \text{NO}_2 \cdot \text{OEt} = \text{HO} \cdot \text{N}_2\text{O} \cdot \text{OH} + \text{Et} \cdot \text{OH}.$
- (3)  $\text{C}_6\text{H}_5 \cdot \text{NH}_2 + \text{NO}_2 \cdot \text{OEt} = \text{C}_6\text{H}_5 \cdot \text{N}_2\text{O} \cdot \text{OH} + \text{Et} \cdot \text{OH}.$
- (4)  $\text{C}_6\text{H}_5 \cdot \text{NH}_2 + \text{NO}_2 \cdot \text{C}_6\text{H}_5 = \text{C}_6\text{H}_5 \cdot \text{N}_2\text{O} \cdot \text{C}_6\text{H}_5 + \text{H}_2\text{O}.$

Each of the reactions (1) and (3) leads to the formation of isomeric products.

T. H. P.

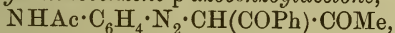
**Decomposition of Azo-compounds by Sodium Hyposulphite** EUGÈNE GRANDMOUGIN (*Ber.*, 1906, 39, 2494—2497).—Sodium hyposulphite is a very convenient reducing agent for azo-compounds in boiling aqueous or alcoholic solutions. Azobenzene gives a quantity

tive yield of hydrazobenzene;  $\alpha$ -nitroso- $\beta$ -naphthol forms  $\alpha$ -amino- $\beta$ -naphthol-4-sulphonic acid (Böniger, Abstr., 1894, i, 199); Orange II, benzeneazo- $\beta$ -naphthol, and benzeneazo- $\alpha$ -naphthol yield the corresponding aminonaphthols.

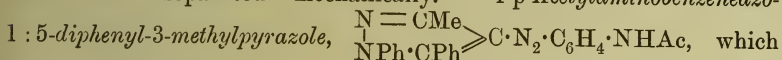
2-Amino- $\alpha$ -naphthol forms a *diacetyl* derivative which crystallises in white needles, melts at  $116^\circ$ , and by partial hydrolysis yields the *N*-acetyl compound, which has been previously described (compare Abstr., 1892, 861). C. S.

[Reduction of Nitroazo-compounds.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 169826).—5-Nitro-2-amino-*p*-tolyl methyl ether,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{OMe}) \cdot \text{NH}_2$ , when diazotised and combined with 7-amino- $\alpha$ -naphthol-3:6-disulphonic acid in alkaline solution, yields a nitroazo-derivative which, when gently warmed with aqueous sodium sulphide, yields an aminoazo-compound giving bluish-black shades on wool in an acid-bath. Other nitroazo-colouring matters are reduced under similar conditions. G. T. M.

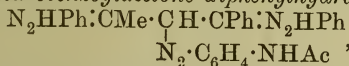
Mixed Disazo-compounds from *p*-Phenylenediamine with Heterocyclic Side-chains. CARL BÜLOW and FRITZ BUSSE (Ber., 1906, 39, 2459—2466).—When benzoylacetone reacts in alcoholic solution with the diazonium compound obtained from acetyl-*p*-phenylenediamine, *p*-acetylaminobenzene-*p*-azobenzoylacetone,



is obtained. It separates from dilute alcohol in golden-yellow needles, melts at  $171^\circ$ , dissolves in dilute alkali to a dark red solution, and is reprecipitated unchanged by carbon dioxide. It reacts with phenylhydrazine in boiling glacial acetic acid to form two products which are separated mechanically. 4-*p*-Acetylaminobenzeneazo-

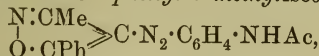


forms orange-red crystals, melts and decomposes at  $229^\circ$  and is insoluble in dilute alkalis. The main product of the reaction is *p*-acetylaminobenzeneazobenzoylacetone diphenylhydrazone,



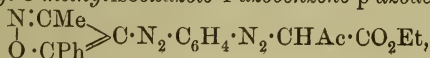
which crystallises in yellow needles and melts at  $206^\circ$ .

4-*p*-Acetylaminobenzeneazo-5-phenyl-3-methylisooxazole,



obtained from acetylaminobenzeneazobenzoylacetone and hydroxylamine in boiling alcoholic solution, separates from alcohol in large, yellow needles, melts and decomposes at  $228^\circ$ , and develops a red coloration with concentrated sulphuric acid. By hydrolysis with alcohol and 10 per cent. sodium hydroxide, 4-*p*-aminobenzeneazo-5-phenyl-3-methylisooxazole,  $\text{C}_{16}\text{H}_{14}\text{ON}_4$ , is obtained, which separates from alcohol in reddish-yellow, glistening needles and melts at  $191^\circ$ .

Ethyl 5-phenyl-3-methylisooxazole-4-azobenzene-*p*-azoacetacetate,



obtained from an alcoholic solution of ethyl acetoacetate and the diazonium salt derived from the preceding compound, in the presence of sodium acetate, forms micro-crystalline, orange needles, melts at  $151^{\circ}$ , and dissolves in hot dilute alkalis with the loss of carbon dioxide.

5-Phenyl-3-methylisooxazole-4-azobenzene-p-4'-azo-1'-phenyl-3'-methyl-5'-pyrazolone, 
$$\begin{array}{c} \text{N}:\text{CMe} \\ | \\ \text{O} \cdot \text{CPh} \end{array} > \text{C} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH} < \begin{array}{c} \text{CMe}:\text{N} \\ | \\ \text{CO}-\text{NPh} \end{array}$$
 is obtained

when phenylhydrazine is slowly added to a glacial acetic acid solution of the preceding compound. It separates from its solution in nitrobenzene after the addition of alcohol or glacial acetic acid in red needles, melts and decomposes at  $205-206^{\circ}$ , dissolves in concentrated sulphuric acid to a reddish-violet solution, but is insoluble in hydrochloric acid or in a solution of sodium hydroxide.

The constitution of this compound has been confirmed by its formation in the reverse order by the following changes: 4-*p*-aminobenzene-azo-1-phenyl-3-methyl-5-pyrazolone (compare Abstr., 1900, i, 261)  $\rightarrow$  1-phenyl-3-methyl-5-pyrazolone-4-azobenzene-p-4'-azobenzoylacetone, which melts and decomposes at  $231-232^{\circ}$ ,  $\rightarrow$  1-phenyl-3-methyl-5-pyrazolone-4-azobenzene-p-4'-azo-3'-phenyl-5'-methylisooxazole, which is identical with the compound previously described. C. S.

[The Diazotisation of Substituted Meta-diamines.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 168299).—2:4-Diaminophenol-6-carboxylic or -sulphonic acid can be readily diazotised to a bisdiazonium salt. Tolylene-2:4-diamine and 4-chloro-*m*-phenylenediamine, on the other hand, do not diazotise readily, for the diazonium salt first formed combines with the still undiazotised diamine to form azo-compounds of the type of Bismarck brown. 2:4-Diaminophenol, which might also be expected to yield azo-derivatives by this secondary reaction, is found, however, to diazotise quite readily in the presence of sufficient mineral acid. The solution of the bisdiazonium salt has a reddish-yellow colour, and the compound combines with the  $\alpha$ -naphtholsulphonic acids (5 and 6), even in acetic acid solutions, to yield an intermediate azodiazazo-product, which in alkaline solutions condenses further with a phenol or phenolsulphonic acid to give rise to a tetrazo-colouring matter. G. T. M.

Occurrence of Glycyl-proline Anhydride in the Tryptic Decomposition Products of Gelatin. PHOEBUS A. LEVENE and WALLACE A. BEATTY (*Ber.*, 1906, 39, 2060—2061).—The compound  $\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2$ , described previously (this vol., i, 469), is readily hydrolysed when heated at  $150^{\circ}$  with concentrated hydrochloric acid. The products obtained are  $\alpha$ -proline [pyrrolidine-2-carboxylic acid] and glycine, and the original substance thus appears to be glycyl-proline anhydride.

J. J. S.

Formation of Dipeptides by the Hydrolysis of Proteids. EMIL FISCHER and EMIL ABDERHALDEN (*Ber.*, 1906, 39, 2315—2320. Compare this vol., i, 326; Levene and Beatty, preceding abstract).—Detailed instructions are given for the isolation of glycyl-l-tyrosine



*anhydride*,  $C_{11}H_{12}O_3N_2$ , from the products of the hydrolysis of silk-fibroin by hydrochloric acid. It separates from hot water in a felted mass of colourless needles, melts and decomposes at  $278-283^\circ$  (corr.), is hydrolysed by 25 per cent. sulphuric acid to tyrosine and glycine, and is identical with the synthetic product in crystalline form, melting point, and solubility, but differs slightly in rotatory power,  $[\alpha]_D$  at  $20^\circ$  being  $123.3^\circ$  as against  $126.4^\circ$ .

*Glycyl-L-leucine anhydride*,  $C_8H_{14}O_2N_2$ , has been isolated from the products of hydrolysis of elastin by 70 per cent. sulphuric acid; it separates slowly from hot alcohol or acetone in microscopic needles, melts at  $253^\circ$  (corr.), has  $[\alpha]_D$   $29.2^\circ$  at  $20^\circ$ , is hydrolysed by concentrated hydrochloric acid at  $100^\circ$  to glycine and leucine, and is identical with the synthetically prepared anhydride.

C. S.

The True Nature of the "Leucines" and "Glucoproteins" obtained by Schützenberger in the Decomposition of Proteid Matter. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1906, 142, 1426—1428).—By fractional precipitation by means of phosphotungstic acid, Schützenberger's leucines, "leuceines," and "glucoproteins" (Abstr., 1877, i, 725; 1879, 542) can be separated into well-known amino-acids; thus, the leucine group  $C_nH_{2n+1}O_2N$  contains 10 per cent. of alanine, 41 per cent. of leucine, 2.8 per cent. of phenylalanine, 1 per cent. of aspartic acid, 0.8 per cent. of glutamic acid, and 5 per cent. of tyrosine; the leucine group  $C_nH_{2n-1}O_2N$  contains 0.27 per cent. of tyrosine, 21 per cent. of alanine, 31 per cent. of leucine, 5.8 per cent. of proline, 19 per cent. of phenylalanine, 3.9 per cent. of aspartic acid, and 1.9 per cent. of glutamic acid; and the glucoprotein group,  $C_nH_{2n}O_4N$ , contains 13 per cent. of alanine, 12 per cent. of leucine, 0.2 per cent. of proline, 7 per cent. of phenylalanine, 5 per cent. of aspartic acid, and 12 per cent. of glutamic acid.

M. A. W.

The "Chlorination" of Wool. LÉO VIGNON and J. MOLLARD (*Compt. rend.*, 1906, 142, 1343—1345).—The authors have examined the action of gaseous chlorine, chlorine water, and bleaching powder, in acid solution on wool, and find that whilst it is dissolved by the prolonged action of the gas, its properties are modified when the action is limited, and it loses 10 per cent. of its weight, is dyed more readily, giving deeper and more brilliant tints, and becomes unshrinkable. The chlorine is not fixed by the wool, but it appears to destroy the projecting points (hooks) of the scales, and thus diminish its aptitude for felting and shrinking; at the same time the increase in the acid and basic functions caused by the rupture of certain linkings of amino-acids would account for the increase in the tinctorial properties.

M. A. W.

Compounds of Nucleic Acid and Proteid, with Special Reference to those in the Mammary Gland and their Relation to Caseinogen Formation. WILHELM LÖBISCH (*Beitr. chem. Physiol. Path.*, 1906, 8, 191—209).—Nucleic acid from the mammary gland in its composition and properties is closely related to the

nucleic acids from the thymus and spermatozoa, and not to guanylic acid. It yields a carbohydrate group. The hypothesis that caseinogen is a simple compound of this acid with the serum proteid is not tenable. The reason for this view and the general theoretical conceptions of the way in which nucleic acid can unite with proteids are discussed.

W. D. H.

**Crystalline Chitosan Compounds from Sepia Shells.** OTTO VON FÜRTH and MICHELE RUSSO (*Beitr. chem. Physiol. Path.*, 1906, 8, 163—190).—Chitosan hydrochloride and hydrobromide can be obtained in characteristic crystalline form. Araki's formula,  $C_{14}H_{26}O_{10}N_2$ , for chitosan is disputed; the molecule is at least twice, perhaps four times, heavier. It contains neither aldehyde nor carboxyl groups, and its nitrogen has the character of a secondary amine. It can combine with one molecule of hydrochloric acid for each atom of nitrogen; the compound is a loose one, and some of the acid is removable in a vacuum. On decomposition with acids, the hydrochloride yields acetic acid 25 and glucosamine 60 per cent. All the glucosamine complexes appear to be acetylated. It takes up one benzoyl group per nitrogen atom. A large part of the oxygen in the molecule is present in hydroxylic form. Chitosan gives with bromine a scarlet additive product from which the bromine is removed by warming with water. The chitosans obtained from the skeletal substance of arthropods and molluscs are identical. The integuments of butterfly pupæ are made of chitin, not of Griffiths' pupin.

W. D. H.

**Action of Light on Enzymes in Oxygen and in Hydrogen, compared with the Action of Photodynamic Substances.** A. JODLBAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, i, 487; from *Arch. Klin. Med.*, 85, 386—394).—Fluorescent substances, even with intense light, only act in presence of oxygen. Sunlight, deprived of ultra-violet rays, will alone injure invertin when oxygen is present. It is probable that photodynamic action consists in a quickening of the simple action of light. This quickening action is very considerable. The effect of sunlight and eosin in concentrations of  $N/2000$  (optimum) in ten minutes was four times as great as that of sunlight, free from ultra-violet rays, in fifteen minutes.

N. H. J. M.

**The Supposed Identity of Pepsin and Rennin.** SIGVAL SCHMIDT-NIELSEN (*Zeit. physiol. Chem.*, 1906, 48, 92—109).—The conclusion is drawn that the enzyme which curdles neutral milk cannot be identical with pepsin.

W. D. H.

## Organic Chemistry.

Reactions of Acetylene with Acidified Solutions of Mercury and Silver Salts. JULIUS A. NIEUWLAND and J. A. MAGUIRE (*J. Amer. Chem. Soc.*, 1906, 28, 1025—1031. Compare Nieuwland, *Abstr.*, 1905, i, 557; Poleck and Thummel, *Abstr.*, 1890, 118; Hofmann, *Abstr.*, 1905, i, 268).—When passed into a solution of mercuric chromate in aqueous chromic acid, acetylene forms a bright yellow *precipitate*,  $\text{CrO}_4\text{Hg}_2\text{C}\begin{smallmatrix} \text{C}\cdot\text{OH} \\ | \\ \text{CH} \end{smallmatrix}$ , which becomes brown when dried,

forms iodoform with moist iodine, especially in alkaline solution, de-flagrates, forming carbon and chromium oxide, when rubbed in a mortar or touched with a hot glass rod, and dissolves in presence of nascent chlorine. With mercuric silicofluoride, acetylene forms a white *precipitate* which turns blue, has an odour of aldehyde, decomposes even when dry, gives the iodoform reaction, reacts energetically with dry bromine or chlorine, and is decomposed by concentrated hydrochloric acid. A similar *precipitate* is formed by the action of acetylene on mercuric fluoroborate.

The white *precipitate* obtained on passing acetylene into a solution of mercuric chlorate in chloric acid is extremely explosive when rubbed, on percussion, or on contact with sulphuric acid, yields acetaldehyde in contact with water, and gives the iodoform reaction in alkaline solution; it decomposes only slowly when moist, attacks organic matter such as paper, and is soluble in acids. A similar *precipitate* is formed with mercuric perchlorate; when pure this is not exploded by heat, friction, or treatment with sulphuric acid. Acetylene and mercuric nitrite interact with development of heat, forming a heavy, cream-coloured *precipitate*,  $\text{C}_2(\text{HgNO}_2)_2$ , which decomposes when heated and gives the iodoform reaction in alkaline solution. Similar white *precipitates* are formed by acetylene with mercury acetamide and mercuric bromate.

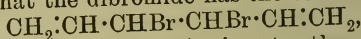
Acetylene forms explosive *precipitates* with silver fluoride, nitrite, silicofluoride, fluoroborate, and bromate in acid solutions and with silver chloride in sodium hyposulphite solution. The *precipitate*,  $3\text{C}_2\text{H}_2, 2\text{H}_3\text{PO}_4, \text{Ag}_3\text{PO}_4, \text{H}_2\text{O}$ , formed from acetylene and silver phosphate in acid solution, is stable, swells and decomposes when heated, is only slowly decomposed when acted on by light, and dissolves in potassium cyanide solution, liberating acetylene. Acetylene does not form *precipitates* with silver chromate or cyanide, but with silver perchlorate it yields an extremely explosive *compound* which is dangerous to prepare even in the smallest quantity. These compounds of silver and acetylene do not give the iodoform reaction, and with the exception of the phosphate are rapidly blackened on exposure to light.

G. Y.



**Derivatives of  $\alpha\gamma\epsilon$ -Hexatriene.** PIETER VAN ROMBURGH and W. VAN DORSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 111—115. Compare this vol., i, 130, 141).—A new preparation of the hydrocarbon,  $\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}\text{:CH}_2$  (by heating the formate of *s*-divinyl glycol), which was purified by fractionation from sodium and finally distilling in an atmosphere of carbon dioxide, boiled at  $77\text{--}78.5^\circ$  under a pressure of 764.4 mm.; it had a sp. gr. 0.749 and  $n_D$  1.4884 at  $13.5^\circ$ .

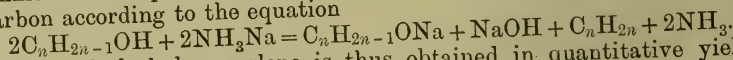
When treated with bromine at  $-10^\circ$ , the dibromide,  $\text{C}_6\text{H}_8\text{Br}_2$ , is obtained as colourless crystals melting at  $85.5\text{--}86^\circ$ ; at higher temperatures a tetrabromide,  $\text{C}_6\text{H}_8\text{Br}_4$ , is obtained, melting at  $114\text{--}115^\circ$ ; at the same time a hexabromide,  $\text{C}_6\text{H}_8\text{Br}_6$ , is always produced, and can be separated by ethyl acetate, and melts at  $163.5\text{--}164^\circ$ . The dibromide and tetrabromide are identical with compounds obtained by Griner by the action of phosphorus tribromide on *s*-divinyl glycol. These facts show that the dibromide has the constitution



and that the addition of the bromine to the hexadiene has not followed Thiele's rule.

When reduced with hydrogen at  $125\text{--}130^\circ$  in the presence of nickel, *n*-hexane is formed. When the hexatriene is reduced with sodium and alcohol, a mixture of hexene and a hexadiene is obtained which could not be resolved into its constituents. It is suggested that the reduction has followed two courses: first a mixture of two hexadienes, the  $\beta\delta$ ,  $\text{CHMe}\text{:CH}\cdot\text{CH}\text{:CHMe}$ , and the  $\beta\epsilon$ ,  $\text{CHMe}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}\text{:CH}_2$ , is produced; the former alone can be further reduced by this method, yielding  $\gamma$ -hexene,  $\text{CH}_2\text{Me}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\text{Me}$ .  
K. J. P. O.

**Reduction of Unsaturated Primary Alcohols of the Fatty Series by Metal-ammonium Compounds.** E. CHABLAY (*Compt. rend.*, 1906, 143, 123—126. Compare Abstr., 1905, i, 502).—The unsaturated primary alcohols of the fatty series react with metal-ammonium compounds to form the corresponding unsaturated hydrocarbon according to the equation



From allyl alcohol, propylene is thus obtained in quantitative yield. The reaction is extremely energetic and is best conducted by allowing the alcohol to fall drop by drop into the solution of the metal-ammonium compound at  $-40^\circ$ . The reaction has also been tried with citronellol, which yields a hydrocarbon boiling at  $168\text{--}169^\circ$  under 760 mm. pressure. It has a sp. gr. 0.789 at  $0^\circ$ , 0.777 at  $22.5^\circ$ ,  $n_D = 1.4484$  at  $22.6^\circ$ . It is probably  $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_3$ , but a small quantity only has been obtained.

It is to be noted that sodium gives both hydrogen and propylene with allyl alcohol, whereas sodammonium yields only the hydrocarbon.  
H. M. D.

**Determination of the Molecular Weights of Alcohols and of Phenols by the Use of Benzoic Anhydride.** ALBERT GASCARD (*J. Pharm. Chim.*, 1906, [vi], 24, 97—101).—When an alcohol or phenol is esterified by means of benzoic anhydride, one molecule of

benzoic acid is formed for each molecule of alcohol or phenol originally taken, according to the equation  $R\cdot OH + (COPh)_2O = Ph\cdot CO_2R + Ph\cdot CO_2H$ , and the molecular weight of the alcohol or phenol can therefore be determined by estimating the benzoic acid present in the resulting mixture. The method of procedure is as follows: about half a gram of the pure alcohol or phenol is placed in a long-necked flask together with two or three times the calculated quantity of benzoic anhydride, the flask is sealed and heated for about twenty-four hours by complete immersion in a bath of water, saturated solution of calcium chloride, or oil, according to the temperature required to complete the esterification; the flask is cooled and opened, and 10 to 20 c.c. pure ether, benzene, or chloroform added to dissolve the mixture of ester, anhydride, and acid; 5 c.c. of water are then added and the acid titrated by means of normal potassium carbonate in the presence of phenolphthalein; the molecular weight ( $P$ ) of the alcohol is given by the equation  $P = p \times 1000/N$ , where  $p$  is the weight of alcohol taken and  $N$  is the number of c.c. of alkali employed. As benzoic anhydride usually contains a little free benzoic acid it is advisable to make a blank experiment to determine the amount; but control experiments show that neither benzoic anhydride nor the ester of a primary or secondary alcohol is appreciably hydrolysed under the conditions of the experiment.

M. A. W.

#### Boiling Points of some Secondary and Tertiary Alcohols.

GUSTAV D. HINRICHS (*Compt. rend.*, 1906, 143, 359—361).—The author has previously shown (this Journal, 1873, 1014) that the boiling point of a compound is a function of its maximum moment of inertia; the secondary and tertiary alcohols,  $C_nH_{2n+1}OH$ , examined by Henry (following abstract), afford a further illustration of this generalisation; their maximum moments of inertia are given below, and the order is the same as that observed by Henry in their boiling points.

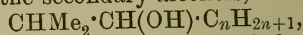
For $n$ .	5.	6.	7.	8.	9.
Tertiary alcohol.....	79	168	309	501	746
Secondary alcohol .....	82	161	286	468	712

M. A. W.

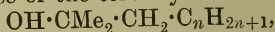
Secondary Alcohols from the Octane,  $CHMe_2\cdot[CH_2]_4\cdot CH_3$ . LOUIS HENRY [with BUELENS and MUSSET] (*Compt. rend.*, 1906, 143, 102—104).—Whilst the secondary alcohols derived from normal octane have approximately the same boiling point, it is found that the boiling points of the various secondary alcohols derived from the  $\beta$ -methyl-octane,  $CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$ , differ considerably. The boiling rises regularly as the distance of the carbinol group from the carbon atom to which the two methyl groups are attached increases. The respective boiling points are  $\gamma$  153—154°,  $\delta$  160—161°,  $\epsilon$  165—166°,  $\zeta$  171—172°.

When the  $\gamma$ -alcohol is converted into the corresponding halogen compound and this is hydrolysed, the tertiary dimethylpentylcarbinol,

$C_5H_{11} \cdot CMe_2 \cdot OH$ , is obtained, and this boils at  $162^\circ$ , which is considerably higher than the boiling point of the secondary  $\gamma$ -alcohol. If the boiling points of the secondary alcohols,



are compared with those of the tertiary alcohols,



it is found that the relationship between the boiling points changes as the number of carbon atoms in the molecule increases. In the case of pentane and hexane the secondary alcohol boils  $10^\circ$  and  $6^\circ$  respectively above the tertiary alcohol; the alcohols derived from heptane have the same boiling point, whilst in the case of octane the tertiary alcohol boils  $8^\circ$  higher than the corresponding secondary compound.

H. M. D.

**Transformation of Secondary-tertiary  $\alpha$ -Glycols into Ketones and the Transposition of Hydrobenzoin.** MARC TIFFENEAU and DORLENCOURT (*Compt. rend.*, 1906, 143, 126—128).— $\gamma$ -Ethylpentylene  $\beta\gamma$ -glycol, obtained by the action of magnesium ethyl bromide on ethyl lactate, boils at  $194$ — $197^\circ$  under the ordinary pressure and has a sp. gr. 0.957 at  $20^\circ$ . When heated with sulphuric acid it yields diethylacetone. *aa*-Diphenylpropylene  $\alpha\beta$ -glycol melts at  $96^\circ$ , and in the same way yields diphenylacetone melting at  $45$ — $47^\circ$ , which gives a *semicarbazone* of melting point  $165$ — $166^\circ$ .

$\alpha$ -Phenyl- $\beta$ -ethylbutylene  $\alpha\beta$ -glycol, which melts at  $89^\circ$ , is converted by sulphuric acid into phenyl isopentyl ketone,  $C_6H_5 \cdot CO \cdot CHEt_2$ . This boils at  $230$ — $236^\circ$  and yields a *semicarbazone* melting at  $179^\circ$ .

Methylhydrobenzoin, melting at  $104^\circ$ , is converted into methyl deoxybenzoin, which boils at  $193^\circ$  under 25 mm. pressure and gives a *semicarbazone* melting at  $194^\circ$ .

In the same way ethylhydrobenzoin, melting at  $117^\circ$ , yields ethyl deoxybenzoin, the *semicarbazone* of which melts at  $167^\circ$ .

These changes are quite analogous to the formation of diethylacetone and diphenylacetone from ethylpentylene glycol and diphenylpropylene glycol respectively, and the intramolecular transposition which takes place in the formation of diphenylacetaldehyde from hydrobenzoin is quite exceptional. The phenomenon of dehydration in the case of glycols of the type  $ArCH(OH) \cdot CH(OH)Ar'$  is therefore different from that of glycols of the general formula  $ArRC(OH) \cdot CH(OH)Ar'$ .

H. M. D.

**Rectification of Official Ethyl Ether.** P. GUIGUES (*J. Pharm. Chim.*, 1906, [vi], 24, 204).—Ethyl ether containing alcohol can be conveniently purified by distillation over colophony, which retains the alcohol. Five per cent. of 98 per cent. alcohol was added to pure anhydrous ether having a sp. gr. 0.720 at  $15^\circ$ , the sp. gr. of the mixture after drying over anhydrous potassium carbonate was 0.725, and this fell to 0.721 after once washing with water; the ether, still retaining 1 per cent. of alcohol, was placed in contact with colophony (50 grams per litre of ether), and finally distilled; the distillate was pure ethyl ether having a sp. gr. 0.720 at  $15^\circ$ .

M. A. W.



**Triformin (Glyceryl Triformate).** PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 109—111).—Although diformin is produced as an intermediate product in the preparation of formic acid from oxalic acid and glycerol, it is difficult to demonstrate the presence of triformin. When a large excess of anhydrous oxalic acid is used and the product distilled under reduced pressure, an oil is obtained which has a sp. gr. 1.309 at 25°, and by titration is shown to consist of 90 per cent. of triformin. Similar results are obtained when pure diformin is treated with anhydrous formic acid. The triformin may be isolated from these mixtures by cooling the oil with liquid ammonia, when crystals separate, which can be freed from liquid. Triformin crystallises in needles melting at 18°, and as a liquid has a sp. gr. 1.320 and  $n_D$  1.4412 at 18°; it boils at 163° under 38 mm. and at 266° under the ordinary pressure. If mixed with diformin, distillation at the ordinary pressure is accompanied by decomposition, carbon monoxide and dioxide being evolved and allyl formate distilling over. On very slow distillation at the ordinary pressure, triformin decomposes into allyl formate, formic acid, and allyl alcohol, which distil, and glycerol which remains in the residue, the oxides of carbon being at the same time evolved.

Triformin is hydrolysed slowly by cold water, but more rapidly by warm water. It reacts with ammonia and amines, yielding the corresponding formamide and glycerol.

K. J. P. O.

**The Fatty Acids of Kephalin.** H. COUSIN (*J. Pharm. Chim.*, 1906, [vi], 24, 101—108. Compare Koch, this vol., ii, 136).—Kephalin, precipitated by alcohol from an ethereal extract of dried ox's brain and purified by repeated treatment with boiling alcohol, forms a firm, waxy, pale yellow mass, becoming reddish-brown with time; it is insoluble in water or acetone, slightly soluble in ethyl acetate or cold alcohol, soluble in hot alcohol; it contains from 3.73 to 3.89 per cent. of phosphorus and 1.82 to 1.86 per cent. of nitrogen, which correspond with the ratios P:N=2.0 to 2.12. The nitrogen bases were removed by partial hydrolysis by heating with a dilute hydrochloric acid, and the residual mixture of fatty acids and glycerophosphoric esters completely saponified by prolonged boiling with an alcoholic solution of potassium hydroxide in alcohol. The glycerophosphoric acid was isolated in the form of its calcium salt, and the mixture of fatty acids, having an iodine value 96 to 102, was separated according to the method previously employed in the case of lecithin (*Abstr.*, 1903, i, 675; this vol., i, 330) into unsaturated and saturated acids. The unsaturated acid or acids (Thudichum's "kephalic acid") is either linoleic acid or a mixture of acids belonging to this series, and stearic acid is the only saturated acid.

M. A. W.

**Constitution of Phenylangelicalactone and isoOctenelactone.** JOHANNES THIELE and WILHELM WEDEMANN (*Annalen*, 1906, 347, 132—142).—It has been shown by Fittig that both the  $\Delta^1$  and  $\Delta^2$  crotonolactones yield the same  $\gamma$ -ketonic acid. Two such lactones, phenylangelicalactone and iso-octenelactone, have been here demonstrated to have the  $\Delta^1$  constitution.

When phenylangelicalactone,  $\text{CH}_2\text{Ph}\cdot\text{CH}\langle\text{CH}\rangle_{\text{O}\cdot\text{CO}}\text{CH}$ , is oxidised with permanganate in neutral alcoholic solution, *phenyldihydroxyvalerolactone*,  $\text{CH}_2\text{Ph}\cdot\text{CH}\langle\text{CH}(\text{OH})\rangle_{\text{O}\cdot\text{CO}}\text{CH}\cdot\text{OH}$ , is obtained, crystallising in needles melting at  $124^\circ$ . With acetyl chloride, it yields a *diacetyl* derivative,  $\text{C}_{15}\text{H}_{16}\text{O}_6$ , as a thick oil, and with *p*-nitrobenzoyl chloride, a *p*-nitrobenzoate,  $\text{C}_{25}\text{H}_{18}\text{O}_{10}\text{N}_2$ , which crystallises in needles melting at  $130^\circ$ . On hydrolysis with barium hydroxide, the barium salt of trihydroxyphenylvaleric acid is formed; the *silver* salt is an amorphous precipitate.

*iso*Octenelactone,  $\text{CH}_2\text{Pr}^\beta\cdot\text{CH}\langle\text{CH}\rangle_{\text{O}\cdot\text{CO}}\text{CH}$ , is prepared by the action of anhydrous sodium acetate on  $\beta\gamma$ -dibromo*isooctenoic* acid, and is an oil of pleasant odour. When oxidised, it yields  $\alpha\beta$ -*dihydroxy-γ-iso-butylbutyrolactone*,  $\text{CH}_2\text{Pr}^\beta\cdot\text{CH}\langle\text{CH}(\text{OH})\rangle_{\text{O}\cdot\text{CO}}\text{CH}\cdot\text{OH}$ , which crystallises in needles melting at  $124^\circ$ . The *di-p*-nitrobenzoate,  $\text{C}_{22}\text{H}_{20}\text{O}_{10}\text{N}_2$ , melts at  $147^\circ$ . On hydrolysis, it yields  $\alpha\beta\gamma$ -trihydroxy- $\gamma$ -*isobutylbutyric* acid, the *silver* salt of which was analysed. K. J. P. O.

**Reactions between Acid Chlorides and Potassium Ethylxanthate.** OSWIN W. WILLCOX (*J. Amer. Chem. Soc.*, 1906, 28, 1031—1034).—The action of acetyl chloride on potassium ethylxanthate in cooled dilute ethereal solution leads to the formation of the mixed *anhydride*,  $\text{OEt}\cdot\text{CS}\cdot\text{SAc}$ , which is obtained as an unstable oil, decomposing when heated into ethyl acetate, carbon disulphide, and other products. In presence of a small amount of ether and without cooling, the action leads to the formation of ethylxanthic anhydride. Only a small amount of this could be obtained from the product of the action of ethyl chlorocarbonate on potassium ethylxanthate.

*Ethyl pentathiotricarbonate*,  $\text{CS}(\text{S}\cdot\text{CS}\cdot\text{OEt})_2$ , is formed by the action of thiocarbonyl chloride on potassium ethylxanthate in ice-cooled aqueous solution, or together with a yellowish-brown oil in acetone solution; it separates from benzene in white, microscopic crystals, melts and decomposes at  $160^\circ$ , and is stable towards dilute acids or alkali hydroxides, but is decomposed, depositing sulphur, when heated with concentrated sulphuric acid.

Large amounts of ethylxanthic anhydride are isolated from the product of the action of carbonyl chloride on potassium ethylxanthate in toluene solution. G. Y.

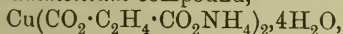
***iso*Succinic Acid.** RICHARD MEYER and PAUL BOCK (*Annalen*, 1906, 347, 93—105).—The preparation of ethyl *isosuccinate* from ethyl  $\gamma$ -bromopropionate and potassium cyanide is unsatisfactory. Attempts to employ Grignard's reaction by treating ethyl  $\gamma$ -bromopropionate successively with magnesium and carbon dioxide were unsuccessful. It was found that the purification of the product of the malonic ester synthesis by conversion of the impure ethyl *isosuccinate* into the crystallisable amide afforded the best results.

*Benzyl isosuccinate* is an oil; the *p*-nitrobenzyl ester, prepared from

impure silver *isosuccinate* and *p*-nitrobenzyl iodide, crystallises in six-sided plates melting at 75°, but cannot be readily converted into *isosuccinic acid*. The *anilide* of *isosuccinic acid* is obtained by heating the ester with aniline, and crystallises in needles melting at 180—181°.

*isoSuccinamide* is easily hydrolysed by boiling with dilute aqueous sodium hydroxide. The acid, which crystallises in white needles, melts at 127—130° and forms a 50.61—50.87 per cent. solution in water at 15°. Its molecular heat of combustion was found to be 365.3 Cal. (constant volume), a number in near agreement with Stohmann's value.

Cadmium *isosuccinate* crystallises with H<sub>2</sub>O in sparingly soluble needles. The *cupro-ammonium* compound,



prepared from ammonium *isosuccinate* and copper acetate, forms bluish-green crystals. *isoSuccinyl chloride*, prepared from thionyl chloride and *isosuccinic acid* or, better, sodium *isosuccinate*, is a liquid boiling at 75° under 50 mm. pressure. Bromo*isosuccinic acid*, prepared from the pure *isosuccinic acid*, forms large, transparent crystals, apparently octohedral, and melts and decomposes at 165—170°.

K. J. P. O.

### Esterification of Unsymmetrical Di- and Poly-basic Acids.

XIV. *i*-Aspartic Acid. RUDOLF WEGSCHEIDER and ERICH FRANKL (*Monatsh.*, 1906, 27, 487—501. Compare Wegscheider, this vol., ii, 77).—As stated by Piutti (Abstr., 1888, 677; 1889, 383), the esterification of *i*-aspartic acid by means of alcohol and hydrogen chloride leads to the formation of  $\beta$ -ethyl hydrogen *i*-aspartate, together with traces of the diethyl ester (compare Curtius and Koch, Abstr., 1885, 885; Fischer, Abstr., 1901, i, 192).

The action of silver nitrate on ammonium *i*-aspartate in aqueous solution leads to the formation of the salt, C<sub>4</sub>H<sub>6</sub>O<sub>7</sub>N<sub>2</sub>Ag<sub>2</sub>. A salt of approximately the constitution C<sub>4</sub>H<sub>5</sub>O<sub>4</sub>Na<sub>2</sub> is obtained in presence of an excess of ammonia; when treated with ethyl iodide, this yields ethyl *i*-aspartate, together with small amounts of an *N*-ethylated product.

The hydrolysis of the diethyl ester by means of a limited amount of alcoholic potassium hydroxide leads to the formation of a mixture of the diethyl ester and *i*-aspartic acid. No ester was obtained on heating potassium hydrogen *i*-aspartate with ethyl iodide and alcohol at 100°. When heated with alcohol in a sealed tube at 93°, *i*-aspartic acid remains unchanged, but at 150—160° it is partially decomposed, yielding carbon dioxide and an oil from which a product could not be isolated.

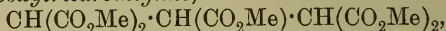
G. Y.

Transformations of Methyl Dicarboxyaconitate. RICHARD ANSCHÜTZ and ALPHONS DESCHAUER (*Annalen*, 1906, 347, 1—16).—Methyl dicarboxyaconitate is best prepared from methyl dichloro-oxalate (1 mol.) and methyl sodiomalonate (3 mols.), when the following reaction takes place:  $\text{OMe} \cdot \text{CCl}_2 \cdot \text{CO}_2\text{Me} + 2\text{CHNa}(\text{CO}_2\text{Me})_2 = 2\text{NaCl} + \text{MeOH} + \text{C}(\text{CO}_2\text{Me})_2 \cdot \text{C}(\text{CO}_2\text{Me})_2 \cdot \text{CH}(\text{CO}_2\text{Me})_2$ . The sodium salt of the methyl dicarboxyaconitate is then formed by interaction



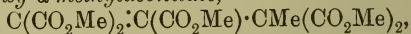
with 1 mol. of methyl sodiomalonate. The ester is purified by recrystallisation from water, and melts at  $62^{\circ}$ . At the same time, *methyl ethylenetricarboxylate*,  $\text{CH}(\text{CO}_2\text{Me})\cdot\text{C}(\text{CO}_2\text{Me})_2$ , is formed as a by-product; it crystallises from methyl alcohol, melts at  $134\text{--}135^{\circ}$ , and does not give a yellow coloration with alkalis as does the aconitate.

*Methyl dicarboxytricarballylate*,



is prepared by reducing methyl dicarboxyaconitate with zinc dust in acetic acid solution, and forms plates melting at  $85\text{--}86^{\circ}$ . It is completely soluble in alkalis and forms the *monosodium* derivative,  $\text{C}_{13}\text{H}_{17}\text{O}_{10}\text{Na}$ . It may also be prepared from methyl dichloroacetate and methyl sodiomalonate. When boiled with concentrated hydrochloric acid it is quantitatively converted into tricarballic acid melting at  $158^{\circ}$ .

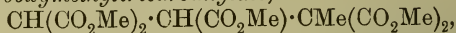
The sodium derivative of methyl dicarboxyaconitate forms small, orange-yellow crystals, and when pure yields with methyl iodide *methyl  $\alpha$ -dicarboxy- $\alpha$ -methylaconitate*,



which crystallises in needles, melts at  $86^{\circ}$ , and boils at  $208\text{--}210^{\circ}$  under 12 mm. pressure.

*$\alpha$ -Methylaconitic acid*,  $\text{CH}(\text{CO}_2\text{H})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , is prepared by heating methyl dicarboxymethylaconitate with 25 per cent. sodium hydroxide at  $60\text{--}70^{\circ}$  and then isolating the methylaconitic acid as the silver salt; it forms small crystals melting and decomposing at  $169\text{--}172^{\circ}$ . The *silver* salt is a white powder.

*Methyl dicarboxymethyltricarballylate*,



is obtained by reducing methyl dicarboxymethylaconitate with zinc dust in acetic acid solution, and forms large, transparent crystals melting at  $58\text{--}59.5^{\circ}$ ; its *sodium* derivative,  $\text{C}_{14}\text{H}_{19}\text{O}_{10}\text{Na}$ , is obtained as a solid by adding dry benzene to its methyl-alcoholic solution. When methyl dicarboxymethylaconitate is boiled with 20 per cent. hydrochloric acid, it is converted into a mixture of two  $\alpha$ -methyltricarballic acids,  $\text{CH}_2(\text{CO}_2\text{H})\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , which are separated by crystallisation from water. The sparingly soluble acid melts at  $178\text{--}180^{\circ}$ , whilst the more soluble acid melts at  $132\text{--}134^{\circ}$ . The *silver* salt of each acid was prepared, and the acids proved to be identical with those obtained by Auwers, Köbner, and Meyenberg (Abstr., 1892, i, 41).

K. J. P. O.

**Synthetical Crystalline *l*-Iditol.** GABRIEL BERTRAND and A. LANZENBERG (*Compt. rend.*, 1906, 143, 291—294).—The authors have obtained 28 grams of pure recrystallised *l*-iditol from 300 grams of xylose by the following modification of Fischer and Fay's method (Abstr., 1895, i, 650); the xylose is converted into a mixture of *l*-gulonic and *l*-idonic acids, the latter removed by crystallisation of its lactone, when the mother liquor reduced by sodium amalgam contains *l*-iditol together with a little *l*-sorbitol, which is removed in the form of its benzylidene derivative, and the crystallisation of the *l*-iditol induced by sowing with a crystal of sorbieritol ( $\alpha$ -iditol) (compare

Maquenne and Bertrand, *Abstr.*, 1901, i, 497). *L*-Iditol crystallises in rhombic prisms, melts at  $73\cdot5^{\circ}$ , and has  $[\alpha]_D + 3\cdot5^{\circ}$  in 10 per cent. aqueous solution at  $20^{\circ}$  [the corresponding constants of *α*-iditol are  $73\cdot5^{\circ}$  and  $-3\cdot5^{\circ}$  respectively, and not  $75^{\circ}$  and  $-3\cdot53^{\circ}$  as originally stated (compare *Abstr.*, 1905, i, 21)]; the *hexa-acetyl* derivative crystallises in hexagonal plates, melts at  $121\cdot5^{\circ}$ , and has  $[\alpha]_D + 25\cdot33^{\circ}$  in 5 per cent. chloroform solution at  $20^{\circ}$  [the *hexa-acetyl* derivative of *α*-iditol melts at  $121\cdot5^{\circ}$  and has  $[\alpha]_D - 25\cdot65^{\circ}$  in 5 per cent. chloroform solution (compare *Abstr.*, 1905, i, 21)]; trimethylene-*L*-iditol crystallises in thin, brilliant needles almost insoluble in alcohol, insoluble in chloroform, soluble in acetic acid, and has  $[\alpha]_D - 30^{\circ}$ , and not  $+8^{\circ}$  as stated by Lobry de Bruyn and Alberda van Eckenstein (*Abstr.*, 1900, i, 332).

M. A. W.

**Action of Ammonium Chloride on Aqueous Sucrose Solutions.** FRIEDRICH STROHMER and O. FALLADA (*Chem. Centr.*, 1906, i, 1819; from *Österr.-ung. Zeit. Zucker-Ind. Landw.*, 35, 168—171).—On heating in various ways aqueous solutions containing sucrose and ammonium chloride in the proportion 3 : 1 or 1 : 1, it is found that the polarisation diminishes to a greater or less extent, the liquid becoming coloured and capable of reducing Fehling's solution. The solution remains neutral, except when heated at  $115^{\circ}$ , in which case it becomes faintly acid. Assuming that the solution contains invert sugar, Clerget's formula indicates an amount of this sugar corresponding very nearly with the original proportion of sucrose. The hydrolysis of the sucrose must be assumed to be a consequence of the decomposition of the ammonium chloride into ammonia and hydrogen chloride.

T. H. P.

**Hydrolysis of Raffinose by means of Citric Acid.** J. PIERAERTS (*Chem. Centr.*, 1906, ii, 24—25; from *Bull. Assoc. chim. Sucr. Dist.*, 23, 1143—1146).—Raffinose is completely resolved into *D*-fructose (lævulose) and melibiose by citric acid, the hydrolytic action of the acid being proportional to its concentration and to the duration of its action. The action of the citric acid may, under certain conditions, proceed further than this first stage, but the lævulose is not attacked until long after the first stage in the hydrolysis of raffinose is reached.

T. H. P.

**Mechanism of Additive Reactions. VII. Reactivity of Unsaturated Nitrogen.** DANIEL VORLÄNDER (*Annalen*, 1906, 345, 251—260).—The oxidation of amines is initially an additive process (compare Dunstan and Goulding, *Trans.*, 1899, 75, 1004; Wolffenstein, *Abstr.*, 1900, i, 209; Bamberger, *Abstr.*, 1902, i, 364). In its subsequent stages, the oxidation is influenced chiefly by the groups containing hydrogen adjacent to the nitrogen atom; consequently primary amines are most slowly, and tertiary amines most rapidly oxidised. Ammonium bases, which do not contain unsaturated nitrogen, are stable towards the oxidising agent. The oxidising agent used in these and the following experiments was permanganic acid in the presence of an acid. The latter on the one hand accelerates the

oxidising action of the permanganate, and on the other retards oxidation by salt-formation with the amine. In neutral or alkaline solution most amines are instantly oxidised by permanganate. The oxidation is also influenced by temperature, concentration, the presence of easily oxidisable substances which act as catalysts, and even by the products of oxidation.

Acyl derivatives are comparatively stable towards alkaline permanganate, but in acid solution are more easily oxidised than the amines, owing to the absence of salt-formation.

These results are illustrated in the paper by tables and curves.

C. S.

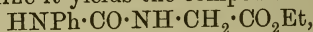
### Oxidation of Ammonia Derivatives by Permanganic Acid.

DANIEL VORLÄNDER, GEORG BLAU, and THEODOR WALLIS (*Annalen*, 1906, 345, 261—276).—The paper gives a detailed account of the results mentioned in the preceding abstract, and is not suitable for abstraction.

The velocity of oxidation of an amine by acidified permanganate under carefully stated conditions is a new constant by which such substances can be identified.

C. S.

**Combination of Amino-acids derived from Proteids.** ALBERT MOREL (*Compt. rend.*, 1906, 143, 119—121).—When the hydrochloride of ethyl glycine is treated with a large excess of carbonyl chloride in boiling toluene, *ethyl glycine isocyanate*,  $\text{CO}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , is formed. It is a colourless liquid which boils at  $115\text{--}120^\circ$  under 15 mm. pressure. With aniline it yields the compound



which melts at  $113\text{--}114^\circ$ . When boiled with water, the *isocyanate* decomposes, carbon dioxide, ethyl alcohol, and carbamidediacetic acid,  $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , being formed. This acid forms well-developed crystals which melt at  $166\text{--}168^\circ$ .

The *isocyanate* reacts with an alkaline solution of leucine, forming the carbamide derivative,



which is insoluble in acids and melts and decomposes at  $183^\circ$ .

In a similar manner, with a solution of tyrosine, the compound  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  is formed; it crystallises from alcohol in delicate needles and melts and decomposes at  $214^\circ$ . These compounds do not appear to be hydrolysed under the influence of pepsin and pancreatic juice.

H. M. D.

**Synthesis of Cyanogen and of Hydrogen Cyanide from their Elements.** THEODOR WALLIS (*Annalen*, 1906, 345, 353—362).—Contrary to statements in the literature, cyanogen is not produced when electric sparks are passed, or the arc is established, between carbon poles in an atmosphere of nitrogen. In the presence of moisture or of hydrogen, hydrogen cyanide is formed.

In order to detect cyanogen in the presence of hydrogen cyanide, the mixture is passed into an acidified solution of a silver salt, the silver cyanide removed, the silver in the solution precipitated by yellow ammonium sulphide, a few drops of alkali are added, and after filtration



and evaporation the test for a thiocyanate is applied. The estimation of cyanogen and hydrogen cyanide is effected by passing the mixture into a solution of potassium hydroxide; the hydrogen cyanide and one-half of the cyanogen is estimated as silver cyanide; the other half, now present as potassium cyanate, is determined by boiling the cyanate with dilute sulphuric acid and titrating the ammonia produced. An alternative method is to pass the mixture into a solution of ammonium hydroxide or carbonate. After titration with a silver solution, the ammonium cyanate is converted into carbamide, and isolated and weighed as such.

Cyanogen prepared in the usual way always contains hydrogen cyanide, which can be removed by passing the gas over cotton-wool moistened with a silver solution.

C. S.

**Action of the Electric Discharge on Cyanogen.** H. GAUDECHON (*Compt. rend.*, 1906, 143, 117—119).—When cyanogen is subjected to the action of the electric discharge, nitrogen is liberated and a solid, brown substance is formed. The composition of the deposit varies with the pressure of the gas, the capacity of the apparatus, and the potential of the discharge. It is partially, sometimes completely, soluble in water and ethyl alcohol, and always dissolves readily in dilute alkali solutions, and therefore does not contain free carbon. When heated carefully to dark redness, the solid substance gives off nitrogen, and the residue is found to be insoluble even in strong alkali solutions. The author points out that the products of the action of the discharge are thus conclusively proved to be condensation products containing excess of carbon, and do not result from the simple polymerisation of cyanogen.

H. M. D.

**Carbonyl Bromide.** A. VON BARTAL (*Annalen*, 1906, 345, 334—353).—Emmerling and Lengyel's (*Abstr.*, 1880, 627) or Besson's (*Abstr.*, 1895, i, 317) methods are unsuitable for the preparation of pure carbonyl bromide. The boron tribromide required in the latter method is conveniently obtained in 60—70 per cent. yield by passing bromine vapour over powdered boron containing 10 per cent. of magnesium at a dull red heat.

Carbonyl bromide is obtained in small quantities directly from carbon monoxide and bromine vapour in the presence of aluminium bromide, or by the silent electric discharge. It is prepared in 50—60 per cent. yield by allowing sulphuric acid of sp. gr. 1.84 to drop slowly into carbon tetrabromide at 160—170°. The red distillate is shaken with mercury, distilled, shaken again with powdered antimony, and once again distilled. Pure carbonyl bromide is a heavy, mobile, colourless liquid which fumes in air, and smells somewhat like phosgene. It boils and decomposes slightly at 64—65°, has a sp. gr. 2.45 at 15°, and is decomposed by light or heat. With dimethylaniline and zinc bromide or aluminium bromide it forms dyes of the crystal-violet group, particularly hexamethyl-*p*-rosaniline hydrobromide; in the absence of the contact substance, *p*-bromodimethylaniline is produced. It is more stable towards water than carbonyl chloride.

C. S.

**Preparation of Cyanamides.** RALPH H. MCKEE (*Amer. Chem. J.*, 1906, 36, 208—213).—Dipropylcyanamide is obtained in a 93 per cent. yield by shaking 1.1 mols. of bromine in light petroleum solution with 1 mol. of dipropylamine and 4.5 mols. of potassium cyanide in aqueous solution below 15°. When heated with sodium methoxide in methyl-alcoholic solution at 65°, it forms *as-ψ-methyl-dipropylcarbamide*,  $\text{OMe}\cdot\text{C}(\text{NH})\cdot\text{NPr}_2$ , which is obtained in a yield of 80 per cent.; it boils at 98° under 19 mm., or at 203° under 748 mm. pressure, has a sp. gr. 0.9103 at 22°/4°, and is more soluble in cold than in hot water.

In a similar manner, diisobutylcyanamide, boiling at 123° under 25 mm. pressure, is obtained in an 83 per cent., diisoamylcyanamide, boiling at 134° under 14 mm. pressure, in a 92 per cent., dimethylcyanamide, boiling at 98° under 104 mm. pressure, in a 50 per cent., ethylcyanamide in a 71 per cent., benzylcyanamide, melting at 43° (33°: Strakosch, this Journal, 1872, 25, 1026), in a 90 per cent., and cyanopiperidine,  $\text{C}_5\text{NH}_{10}\cdot\text{CN}$ , boiling at 102° under 11 mm. pressure, in an 80 per cent. yield. isoAmylcyanamide,  $\text{C}_5\text{H}_{11}\cdot\text{NH}\cdot\text{CN}$ , prepared by this method, was analysed.

Diethylcyanamide is obtained in a good yield if ethyl acetate is used in place of light petroleum, and the temperature maintained about 5°. *as-ψ-Methyldiethylcarbamide*,  $\text{OMe}\cdot\text{C}(\text{NH})\cdot\text{NEt}_2$ , boils at 171—172° under 745 mm. pressure, distils with water, benzene, or ether vapour, is a strong base, and can be titrated with hydrochloric acid. G. Y.

**Constitution of Fulminic Acid.** MILORAD Z. JOVITSCHITSCH (*Annalen*, 1906, 347, 233—247).—The formulæ suggested by various investigators for fulminic acid are discussed, and it is pointed out that Nef's formula,  $\text{C}\cdot\text{NOH}$ , is not in accord with the fact that an unsaturated compound is formed in an extremely violent reaction by the action of nitric acid on alcohol. It is thought rather that Scholl's

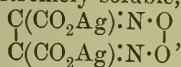
formula,  $\begin{array}{c} \text{CH}\cdot\text{N}\cdot\text{O} \\ | \quad | \\ \text{CH}\cdot\text{N}\cdot\text{O} \end{array}$ , which represents the substance as glyoxime peroxide, is correct, and attempts have been made to synthesise the compound and thus solve the question of its constitution.

From the peroxide of ethyl diisonitrososuccinate (ethyl glyoxime peroxide-dicarboxylate),  $\begin{array}{c} \text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{O} \\ | \quad | \\ \text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{O} \end{array}$ , the silver salt of the dioxime peroxide,  $\begin{array}{c} \text{CAg}\cdot\text{N}\cdot\text{O} \\ | \quad | \\ \text{CAg}\cdot\text{N}\cdot\text{O} \end{array}$ , was obtained. It resembles silver fulminate extremely closely, but differs from it in being easily soluble in nitric acid and in being less explosive.

*Ethyl glyoxime-peroxide-dicarboxylate* (ethyl azodioxazinedicarboxylate) is obtained in quantitative yield by preparing the nitrolic acid of ethyl acetoacetate,  $\text{OHN}\cdot\text{C}(\text{NO}_2)\cdot\text{CO}_2\text{Et}$  (Abstr., 1892, 699), and simply evaporating its ethereal solution, when nitrous acid is eliminated and the peroxide formed.

The corresponding acid is obtained from the ester by dissolving it in concentrated sulphuric acid, and then pouring into water and extract-

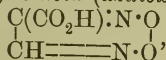
ing the oil which separates with ether; the crystalline acid melts at  $96^{\circ}$ ; its alkali salts are extremely soluble, but the *silver* salt,



is a yellowish-white powder, which is very sensitive to light and somewhat explosive.

In this hydrolysis an oil is also formed which may be an ethyl oximidoacetate,  $\text{OH}\cdot\text{N}\text{:CH}\cdot\text{CO}_2\text{Et}$ .

*Glyoxime-peroxide-carboxylic acid (azdioxazinecarboxylic acid),*



is prepared by hydrolysing the peroxide ester with sulphuric acid and dissolving the insoluble product in sodium hydroxide; it forms a thick, pale syrup, extremely soluble in water, and when treated with silver nitrate yields a yellow, extremely explosive silver salt, which is not affected by light. When the sodium salt, which is prepared by precipitating the strongly alkaline solution of the acid with alcohol, is

treated with silver nitrate, the *silver* salt,  $\begin{array}{c} \text{C}(\text{CO}_2\text{Ag})\text{:N}\cdot\text{O} \\ | \\ \text{C}\text{Ag}=\text{N}\cdot\text{O} \end{array}$ , is formed, and exceeds all hitherto described salts in explosibility.

The *silver glyoxime peroxide (silver azdioxazine)* is prepared by treating ethyl glyoxime-peroxide-dicarboxylate with 25 per cent. sodium hydroxide under accurately defined conditions; both a *mono-* and a *di-sodium* salt can be obtained, from which both *mono-* and *di-silver* salts are prepared. The *di-silver* salt is a yellow powder which is not sensitive to light and is stable in the air. When treated with concentrated hydrochloric acid or heated on platinum it explodes violently. When boiled for some time with dilute hydrochloric acid, hydroxylamine is formed; but if the salt is dissolved in dilute nitric acid and hydrochloric acid then added, glyoxime peroxide can be isolated.

K. J. P. O.

**Ureides. I. Action of Urethane on Pyruvic Acid and its Derivatives.** LOUIS J. SIMON (*Ann. Chim. Phys.*, 1906, [viii], 8, 467—501).—A more detailed account of work already published (*Abstr.*, 1902, i, 14).

G. S.

**Researches in the cycloHexane Series.** PAUL FREUNDLER (*Bull. Soc. chim.*, 1906, [iii], 35, 539—551).—The results recorded have, for the most part, already appeared (Freundler and Damond, *Abstr.*, 1905, i, 890, and Freundler, this vol., i, 283). The present two papers give experimental details of the methods of preparation employed.

When iodocyclohexane is heated with ethyl sodioacetoacetate in presence of alcohol, only traces of ethyl cyclohexylacetoacetate are produced, the principal product being cyclohexene. When the alcohol is replaced by xylene, scarcely any action occurs.

It was found impossible to prepare pure hexahydrobenzyl chloride by the action of hydrogen chloride or phosphorus pentachloride on the corresponding alcohol. Similar attempts to prepare hexahydrobenzyl bromide were also unsuccessful.



Acetonitrile condenses with magnesium hexahydrobenzyl iodide, yielding methylcyclohexane, a white solid containing nitrogen, and dicyclohexylethane,  $C_{14}H_{26}$ , a viscous, pleasant-smelling liquid, which boils at  $145-150^\circ$  under 20 mm. and at  $263-264^\circ$  under 762 mm. pressure.

A specimen of magnesium hexahydrobenzyl bromide, containing some hexahydrobenzyl alcohol, was condensed with ethyl acetate, and yielded a *product* boiling at  $202-205^\circ$  under 45 mm. pressure, which may be the alcohol  $(C_6H_{11}\cdot CH_2)_2\cdot CMe\cdot OH$ . When warmed with oxalic acid at  $140-150^\circ$ , this was transformed into an unsaturated hydrocarbon, boiling at  $143-147^\circ$  under 12-13 mm. pressure. T. A. H.

**Reduction of Nitro-compounds by Tin Haloids. II.** HEINRICH GOLDSCHMIDT and EINAR SUNDE (*Zeit. physikal. Chem.*, 1906, 56, 1-42. Compare Abstr., 1904, ii, 608).—The method described previously has been further used in the study of *m*- and *o*-nitrophenols, *o*- and *p*-nitrobenzenesulphonic acids, and *o*- and *m*-nitrobenzaldehyde. The behaviour of the nitrophenols and of *m*-nitrobenzaldehyde is normal, but that of the other substances named is not so strictly in harmony with the rules deduced in the earlier paper. In the case of the two nitrobenzenesulphonic acids, it is found that an increase in the hydrochloric acid concentration is accompanied by an increase in the velocity of reduction which is greater than that required by the rule of proportionality (*loc. cit.*). Similar deviations from this rule have been observed in the case of *o*-nitrobenzaldehyde. Further, whilst the other nitro-compounds studied require 3 mols. of stannous salt for each nitro-group, it is found that *o*-nitrobenzaldehyde reacts with 2 mols. of stannous salt, and reduction beyond that stage takes place with extreme slowness, owing to the production of anthranil.

The authors' experiments show that in the reduction of nitro-compounds a part of the hydrochloric acid may be replaced by metallic chlorides without appreciably affecting the velocity of reduction. Thus the rate of reduction of *m*-nitrobenzenesulphonic acid is the same whether the solution is *N*/1 with regard to hydrochloric acid or *N*/2 with regard to hydrochloric acid and, at the same time, *N*/2 with regard to sodium or barium chloride. This observation leads to the view that the ion which is active in all these reduction processes is  $SnCl_3'$  (compare *loc. cit.*).

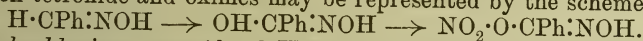
The above-mentioned behaviour of *o*-nitrobenzaldehyde furnishes support to Haber's view of the stages in the reduction of nitro-compounds: namely, (1)  $R\cdot NO_2 \rightarrow R\cdot NO$ , (2)  $R\cdot NO \rightarrow R\cdot NH\cdot OH$ , (3)  $R\cdot NH\cdot OH \rightarrow R\cdot NH_2$ . The authors find that while change (2) takes place apparently in all cases with extreme rapidity, the velocity of change (3), although considerably greater than that of change (1), is measurable in many cases; the laws regulating the velocity of change (3) appear to be similar to those regulating the velocity of change (1). The substitution of  $SnBr_2 + HBr$  for  $SnCl_2 + HCl$ , which makes the reduction change (1) eight times as rapid, makes the reduction change (3) about four times as rapid.

J. C. P.

**New Method of preparing the so-called Primary Dinitro-hydrocarbons.** GIACOMO PONZIO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 42—45 and 118—128).—The ordinary methods for preparing dinitro-derivatives of aliphatic hydrocarbons cannot be employed for obtaining primary dinitrohydrocarbons containing a complicated aromatic group. The latter compounds can, however, be prepared by the action of nitrogen tetroxide on ethereal solutions of the oximes (this vol., i, 593). In this way the author has obtained phenyldinitromethane, *p*-tolyldinitromethane, anisyldinitromethane, and piperonyldinitromethane.

The statement, based on the work of Scholl (Abstr., 1891, 315) and Beckmann (Abstr., 1889, 980), that the action of nitrogen tetroxide on aromatic aldoximes yields peroxides of the aldoximes, which then undergo transformation into peroxides of the dioximes, is erroneous. Only in the cases of benzaldoxime and *p*-tolualdoxime are small proportions of these peroxides formed.

Regarding the primary dinitro-hydrocarbons as nitrohydroxamic acids (Abstr., 1903, i, 786), their formation by the interaction of nitrogen tetroxide and oximes may be represented by the scheme :



*p*-Tolualdoxime peroxide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{N}\cdot\text{O}\cdot\text{O}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$ , prepared as described above, and also by passing nitrous acid vapours into an ethereal solution of *p*-tolualdoxime, crystallises from chloroform in shining, white plates, decomposes with a slight explosion at 121°, and dissolves in benzene.

*p*-Tolildioxime peroxide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}\cdot\text{N}\cdot\text{O}$   
 $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}\cdot\text{N}\cdot\text{O}$ , crystallises from alcohol in shining, white needles, melts at 143°, and dissolves in ether, chloroform, or benzene, and, to a slight extent, in light petroleum.

*p*-Tolyldinitromethane,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{NO}_2)_2$ , crystallises from light petroleum in white plates melting at 77°, and dissolves in all the ordinary organic solvents; when heated at about 130°, it yields *p*-toluic acid. The *potassium* derivative,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NO}_2)_2\cdot\text{NO}_2\text{K}$ , crystallises from alcohol in yellow laminæ and dissolves readily in water. The *silver* derivative,  $\text{C}_8\text{H}_7\text{O}_4\text{N}_2\text{Ag}$ , separates from water in yellow needles and is stable under the action of light.

Anisildioxime peroxide,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N}\cdot\text{O}$   
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N}\cdot\text{O}$ , crystallises from alcohol in shining, white needles, melting at 113°, and dissolves in light petroleum, ether, chloroform, or benzene.

Anisyldinitromethane,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NO}_2)_2$ , crystallises from light petroleum in slender needles, melting at 34°, and dissolves readily in all the ordinary organic solvents; when heated at about 130°, it gives anisic acid. The *potassium* derivative,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NO}_2)_2\cdot\text{NO}_2\text{K}$ , crystallises from water in red laminæ, which, if left in the mother liquor, rapidly change to a mass of yellow prisms. The *silver* derivative,  $\text{C}_8\text{H}_7\text{O}_5\text{N}_2\text{Ag}$ , separates from water in orange-yellow plates, which remain unchanged in the light.

*Piperonyldinitromethane*,  $\text{CH}(\text{NO}_2)_2 \cdot \text{C}_6\text{H}_3 < \text{O} > \text{CH}_2[1:3:4]$ , crystallises from light petroleum in white plates, melts at  $72^\circ$ , and decomposes at about  $130^\circ$  with evolution of red vapours. The *potassium* derivative,  $\text{C}_8\text{H}_5\text{O}_6\text{N}_2\text{K}$ , forms yellow prisms, soluble in water and sparingly so in alcohol.

The *silver* derivative,  $\text{C}_8\text{H}_5\text{O}_6\text{N}_2\text{Ag}$ , crystallises from water in red needles stable towards light. T. H. P.

**Hydrolysis of Methyl Benzenesulphonate.** II. ARTUR PRAETORIUS (*Monatsh.*, 1906, 27, 465—485. Compare Abstr., 1905, i, 186).—The hydrolysis of methyl benzenesulphonate by water, as also its conversion into a methyl haloid and benzenesulphonic acid by the action of a hydrohaloid acid or its salts, are side-reactions. Of these the latter is a reaction of the halogen anion, as is shown by the equivalence of the amounts of the products, and it is not accelerated by the presence of hydrogen ions.

The results obtained agree with Wegscheider's formula for the hydrolysis of esters (Abstr., 1902, ii, 493). G. Y.

**Nitration of Aromatic Arylsulphonamides.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 163516).—The nitro-derivatives of aromatic arylsulphonamides formerly described (Abstr., 1905, i, 639) are readily obtained by nitrating in the presence of a suitable organic solvent, such as alcohol, acetone, or benzene. When the solvent is not miscible with nitric acid, vigorous agitation is necessary.

C. H. D.

**Preparation of Hydroxyethylaniline and its Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 163043).—Hydroxyethylaniline and similar compounds are obtained in good yield by heating aromatic amines with ethylene chlorohydrin and water. One mol. of the chlorohydrin and 2 mols. of the amine may be used, or the excess of the latter may be replaced by sodium acetate or carbonate. Thus aniline yields hydroxyethylaniline (Knorr, Abstr., 1889, 1218).

*Hydroxyethylaniline-o-carboxylic acid*,



prepared from anthranilic acid, crystallises from benzene in needles and melts at  $143^\circ$ .

*Hydroxyethyl-o-toluidine*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , forms a colourless oil and boils at  $285$ — $286^\circ$ . C. H. D.

**Compounds of Wool with Colourless Amines and Acids.** DANIEL VORLÄNDER and A. J. PEROLD (*Annalen*, 1906, 345, 288—302).—The absorption of amines and acids by wool is similar to other chemical additive processes. In the series aniline, chloroaniline, and dichloroaniline hydrochlorides, the amount of the absorption is in the same order as the dissociation of the salt. The same holds true after the addition of hydrochloric acid, acetic acid, or acetic acid and sodium acetate, the absorption of amine being greatest in the last case.

The absorption of different acids is not in the order of their



relative strengths, probably because in a heterogeneous system adsorption, diffusion, capillarity, &c., play a part in the additive process. With acids of similar chemical character, however, the amount of absorption is in the order of their conductivities.

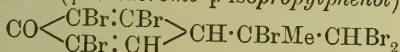
Neutral salts are not absorbed by wool, but potassium hydroxide, tetramethylammonium hydroxide, and *p*-benzeneazophenyltrimethylammonium hydroxide are very readily taken up.

There is not any essential difference between the absorption by wool or silk of coloured and colourless substances.

Extensive tables are given in the paper.

C. S.

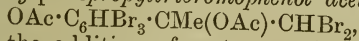
Action of Bromine and Chlorine on Phenols. Substitution Products,  $\psi$ -Bromides, and  $\psi$ -Chlorides. XVI. Hexabromo- $\psi$ -bromide of *p*-isoPropylphenol. THEODOR ZINCKE (*Annalen*, 1906, 349, 67—82. Compare this vol., i, 172).— $\psi$ -*p*-Tribromoiso-propyltribromophenol ( $\psi$ -hexabromo-*p*-isopropylphenol),



or  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CBrMe} \cdot \text{CHBr}_2$ , is obtained by treating finely-powdered 3:5:3':5'-tetrabromo-*p*-diphenoldimethylmethane (*loc. cit.*) with a slight excess of bromine for twenty-four hours. It crystallises in colourless plates or prisms and melts at 115—116°. Cold solutions of sodium hydroxide or carbonate do not react appreciably; water acting on the substance in acetone produces pentabromoisopropylidenequinone. Cold acetic anhydride and concentrated sulphuric acid produce the *acetyl* derivative,  $\text{C}_{11}\text{H}_8\text{O}_2\text{Br}_6$ , which melts at 133—134° and is easily hydrolysed in cold alcoholic solution, yielding by loss of hydrogen bromide pentabromo-*p*-isopropylphenol (see below). When the  $\psi$ -hexabromide is boiled with acetic anhydride it yields tetrabromo-*p*-isopropenylphenol acetate (see below), in addition to the normal *acetyl* derivative.

*p*-Dibromoisopropylidenetribromoquinone (*pentabromoisopropylidenequinone*),  $\text{CO} \begin{array}{c} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CH} \end{array} \text{C}:\text{CMe} \cdot \text{CHBr}_2$ , is prepared by shaking an ethereal solution of the  $\psi$ -hexabromide with an equal volume of 10 per cent. sodium acetate, or as above. It separates from ether in glistening, golden-yellow needles and melts at 143—144°, and with hydrogen bromide regenerates the  $\psi$ -hexabromide.

*a*-Dibromo- $\beta$ -acetoxy-*p*-isopropyltribromophenol acetate,



is precipitated by the addition of water to the colourless solution obtained by treating the preceding quinone with cold acetic anhydride and concentrated sulphuric acid. It separates from methyl alcohol in thick, glistening, rhombic plates, melts at 127°, and by hydrolysis yields *p*-dibromoisopropenyltribromophenol (*pentabromo-p*-isopropenylphenol),  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CMe}:\text{CHBr}_2$ , which melts at 143—144°. The last-mentioned compound is also obtained when the isomeric quinone is allowed to remain in acetone or is reduced by alkaline stannous chloride; the *acetyl* derivative,  $\text{C}_{11}\text{H}_7\text{O}_2\text{Br}_5$ , melts at 104—105°.

*p*-Bromoisopropenyltribromophenol (*tetrabromo-p*-isopropenylphenol),  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CMe}:\text{CHBr}$ , is obtained by the hydrolysis of the

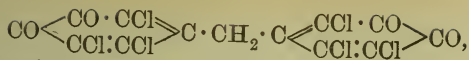
tetrabromoacetate prepared from the  $\psi$ -hexabromide, or by the reduction of the pentabromoquinone by stannous chloride in glacial acetic acid. It crystallises in colourless needles, melts at 98—99°, combines with bromine to form, in the cold the  $\psi$ -hexabromide, or at 100° the  $\psi$ -heptabromide (*loc. cit.*); its acetyl derivative separates from alcohol in rhombic leaflets, melts at 126—127°, and is identical with the acetate obtained from the  $\psi$ -hexabromide by boiling acetic anhydride. C. S.

**Action of Tertiary Amines on Tetrachloro- $p$ -cresol  $\psi$ -Bromide.**  
**XVII.** THEODOR ZINCKE and L. HUNKE (*Annalen*, 1906, 349, 83—98).—2:3:5:6-Tetrachloro-4-hydroxybenzylpyridinium bromide,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_5\text{Br}$ , obtained from tetrachloro- $p$ -cresol  $\psi$ -bromide and pyridine in ethereal solution, separates from hot glacial acetic acid in leaflets and melts and decomposes at 231°. It forms with bromine water in acetic acid glistening, yellow leaflets of a *perbromide*, with potassium dichromate a yellow, crystalline precipitate, and with potassium iodide a violet-brown, glistening *periodide*. The *platini-chloride*,  $(\text{C}_{12}\text{H}_7\text{ONCl}_4)_2 \cdot \text{H}_2\text{PtCl}_6$ , forms yellow crystals.

The betaine derivative of 2:3:5:6-tetrachloro-4-hydroxybenzyltrimethylammonium hydroxide,  $\text{C}_6\text{Cl}_4 \left\langle \begin{smallmatrix} \text{O} \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{NMe}_3$ , results when tetrachloro- $p$ -cresol  $\psi$ -bromide in ether is treated with the calculated quantity of 30 per cent. aqueous trimethylamine. It forms a white, crystalline powder, melts and decomposes at 186°, is stable towards aqueous alkali hydroxides, but is converted by hot alcoholic solutions into tetrachloro- $p$ -hydroxybenzyl ethyl ether (*Abstr.*, 1902, i, 282).

2:3:5:6-Tetrachloro-4-hydroxy-4'-diethylaminodiphenylmethane hydrobromide,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NEt}_2 \cdot \text{HBr}$ , is obtained when the  $\psi$ -bromide is treated with a small excess of diethylaniline in ether, and forms white needles which melt and turn red at 257—258°. The free base,  $\text{C}_{17}\text{H}_{17}\text{ONCl}_4$ , melts at 135° and forms the corresponding salts with hydrogen chloride or bromide in glacial acetic acid. The base is stable towards hot hydrochloric acid, and is decomposed by hot dilute alkalis, diethylaniline and tarry products being formed. The *acetyl* compound forms colourless needles and melts at 120°.

Octachloro- $p$ -diphenolmethane,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{Cl}_4 \cdot \text{OH}$ , is obtained by the action of 5 per cent. sodium hydroxide on tetrachloro- $p$ -cresol  $\psi$ -bromide, of water at 130—140°, or of 5—20 per cent. sodium hydroxide on the pyridinium bromide (with 1 per cent. sodium hydroxide the chief product is tetrachloro- $p$ -hydroxybenzyl alcohol), or of concentrated sulphuric acid on tetrachloromethylenequinone, tetrachlorotoluquinol, or the isomeric tetrachloro- $p$ -hydroxybenzyl alcohol (compare *Abstr.*, 1902, i, 282; 1903, i, 760, in which the product is regarded as a derivative of dihydroxystilbene). Octachloro- $p$ -diphenolmethane forms colourless needles and melts at 279°; and the *acetyl* derivative,  $\text{C}_{17}\text{H}_8\text{O}_4\text{Cl}_8$ , at 257—258°. Nitric acid of sp. gr. 1.4 in glacial acetic acid solution converts the diphenolmethane into tetrachloro- $p$ -quinone, whereas with acid of sp. gr. 1.5 at a gentle heat the chief product is an *o*-quinone,



which separates from benzene in dark red crystals and dissolves in alkalis with a greenish-blue colour changing to brown (compare Abstr., 1899, i, 616).

Bromine at 150° reacts with the diphenolmethane to form a mixture of substances which melts at 261° and behaves like a  $\psi$ -bromide.

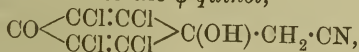
C. S.

**Tetrachloro- $\psi$ -cresol- $\psi$ -chloride. XVIII.** THEODOR ZINCKE and KARL BÖTTCHER (*Annalen*, 1906, 349, 99—106. Compare Abstr., 1902, i, 282; this vol., i, 166).—*Tetrachloro- $\psi$ -cresol- $\psi$ -chloride*,  
 $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2\text{Cl}$

or  $\text{CO} \begin{array}{c} \text{CCl} : \text{CCl} \\ \text{CCl} : \text{CCl} \end{array} \text{CH} \cdot \text{CH}_2\text{Cl}$ , results when tetrachloro- $\psi$ -hydroxybenzyl alcohol is heated at 100° with an excess of hydrogen chloride in glacial acetic acid, or by chlorinating tetrachloro- $\psi$ -cresol at 150—180°. It crystallises in long needles, melts at 145—146°, and behaves like the corresponding  $\psi$ -bromide (*loc. cit.* and preceding abstract). The *acetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2\text{Cl}$ , melts at 118—119°, and by boiling with acetic anhydride and sodium acetate yields the diacetate of tetrachloro- $\psi$ -hydroxybenzyl alcohol.

$\omega$ -2:3:5:6-Pentachlorotolu- $\psi$ -quinol,  $\text{CO} \begin{array}{c} \text{CCl} : \text{CCl} \\ \text{CCl} : \text{CCl} \end{array} \text{C}(\text{OH}) \cdot \text{CH}_2\text{Cl}$ , obtained from the  $\psi$ -chloride by the action of nitric acid of sp. gr. 1.4, forms colourless needles, melts at 137—138°, is soluble in alkali hydroxides, and by warming with sodium carbonate yields the oxide described previously (Abstr., 1902, i, 283). The *acetyl* compound,  $\text{C}_9\text{H}_5\text{O}_3\text{Cl}_5$ , forms colourless needles and melts at 128°.

*Tetrachloro- $\psi$ -hydroxybenzyl cyanide*,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{CN}$ , obtained from the  $\psi$ -chloride and potassium cyanide in aqueous acetone, separates from dilute acetic acid in leaflets or needles, melts at 208—210°, yields an *acetyl* compound melting at 140—142°, and is hydrolysed by dilute sulphuric acid (3:2) at 170—180°, yielding *tetrachloro- $\psi$ -hydroxyphenylacetic acid*,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which melts and decomposes at 240—242°. The cyanide is converted by nitric acid of sp. gr. 1.51 into the  $\psi$ -quinol,



which crystallises in needles, melts and decomposes at 200—202°, and yields an *acetyl* derivative which melts and decomposes at 168°.

C. S.

**Bromine Derivatives of  $\psi$ -Hydroxystilbene. XIX.** THEODOR ZINCKE and W. GEIBEL (*Annalen*, 1906, 349, 107—123).— *$\psi$ -Hydroxy- $\alpha$ -phenylcinnamic acid*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CPh} \cdot \text{CO}_2\text{H}$ , is obtained from  $\psi$ -hydroxybenzaldehyde, sodium phenylacetate, and acetic anhydride, the resulting *acetyl* compound being hydrolysed. The acid forms small, white needles, melts at 223° with loss of carbon dioxide, and gives an *acetyl* derivative,  $\text{C}_{17}\text{H}_{14}\text{O}_4$ , which melts at 174°; the *methyl* ester melts at 168—169°, and its *acetyl* derivative,  $\text{C}_{18}\text{H}_{16}\text{O}_4$ , at 108°.

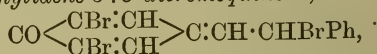


*p*-Hydroxystilbene,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHPh}$ , results when the preceding acid is heated rapidly to its melting point; unchanged acid is removed by sodium carbonate, and the residue, after treatment with dilute acid, is crystallised from benzene or glacial acetic acid. It separates in white leaflets, melts at  $189^\circ$ , and forms sparingly soluble *sodium* and *potassium* salts; the *acetyl* compound,  $\text{C}_{16}\text{H}_{14}\text{O}_2$ , melts at  $152^\circ$ .

3:5-Dibromo-4-hydroxystilbene  $\psi$ -dibromide,  
 $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CHBr}\cdot\text{CHBrPh}$

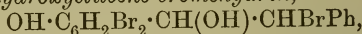
or  $\text{CO}\left\langle\begin{smallmatrix}\text{CBr}\cdot\text{CH} \\ \text{CBr}\cdot\text{CH}\end{smallmatrix}\right\rangle\text{CH}\cdot\text{CHBr}\cdot\text{CHBrPh}$ , obtained from bromine and *p*-hydroxystilbene in glacial acetic acid, crystallises in white needles, darkens at  $192^\circ$ , and melts and decomposes at  $201^\circ$ . With methyl or ethyl alcohol it yields an oily product,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{OR})\cdot\text{CHBrPh}$  (where  $\text{R} = \text{Me}$  or  $\text{Et}$ ). The *acetyl* derivative,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{Br}_4$ , obtained with acetic anhydride and concentrated sulphuric acid, forms glistening leaflets and melts at  $182^\circ$ .

1-Bromophenylethylidene-3:5-dibromoquinone,



formed spontaneously from the  $\psi$ -bromide in aqueous acetone, or in ethereal solution by the action of 10 per cent. aqueous sodium acetate, is an amorphous, yellow powder, which sinters at  $140^\circ$  and melts and decomposes at  $190^\circ$ ; with hydrogen bromide in glacial acetic acid the  $\psi$ -bromide is regenerated.

3:5-Dibromo-4-hydroxystilbene bromohydrin,



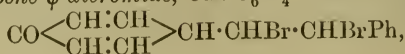
results by the slow addition of water to the  $\psi$ -bromide in acetone; it crystallises in white needles, melts at  $170^\circ$ , and with acetic anhydride and sulphuric acid yields the *diacetate* described subsequently.

The *acetyl* compound,  $\text{CO}\left\langle\begin{smallmatrix}\text{CBr}\cdot\text{CH} \\ \text{CBr}\cdot\text{CH}\end{smallmatrix}\right\rangle\text{CH}\cdot\text{CH}(\text{OAc})\cdot\text{CHBrPh}$ , obtained by shaking the  $\psi$ -bromide with sodium acetate and glacial acetic acid, forms a white powder, melts at  $135^\circ$ , yields the preceding compound on hydrolysis, and by treatment with sodium acetate and acetic anhydride forms the *diacetate*,  $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{OAc})\cdot\text{CHBrPh}$ , which melts at  $142\text{--}143^\circ$ .

3:5-Dibromo-4-hydroxystilbene,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}\cdot\text{CHPh}$ , obtained from the  $\psi$ -bromide in acetone with excess of stannous chloride, crystallises in needles, melts at  $150^\circ$ , forms sparingly soluble salts with alkalis, yields an *acetyl* compound which melts at  $130\text{--}131^\circ$ , and regenerates the  $\psi$ -bromide by treatment with bromine in glacial acetic acid.

The *pyridinium* bromide,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{C}_5\text{NH}_5\text{Br})\cdot\text{CHBrPh}$ , formed from the  $\psi$ -bromide and pyridine in ether, melts at  $145\text{--}165^\circ$ . It dissolves easily in alcohol, acetone, or glacial acetic acid, but quickly separates in the form of a white, sparingly soluble, crystalline powder, which melts and decomposes at  $194^\circ$ . Alkalis decompose it, yielding pyridine and an amorphous, red substance.

*p*-Hydroxystilbene  $\psi$ -dibromide,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBrPh}$  or



is prepared by the action, in the dark, of the requisite quantity of bromine in ether on *p*-hydroxystilbene in ether at  $-15^{\circ}$ ; it is an unstable, white powder which turns brown at  $155^{\circ}$ , melts and decomposes at  $161^{\circ}$ , and does not readily yield pure derivatives. The *acetate*, obtained by acetic anhydride and sulphuric acid, crystallises well in needles and melts and decomposes at  $190-192^{\circ}$ , decomposition beginning at  $180^{\circ}$ . The *quinone*,  $\text{CO} \begin{smallmatrix} \text{CH}:\text{CH} \\ \text{CH}:\text{CH} \end{smallmatrix} \text{C}:\text{CH}\cdot\text{CHBrPh}$ , obtained in a similar manner to the preceding quinone, is an amorphous, yellow powder, becoming white in air; it is readily soluble in the usual solvents, but cannot be crystallised. By reduction with stannous chloride in acetone it yields *p*-hydroxystilbene. The *pyridinium bromide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_5\text{NH}_5\text{Br})\cdot\text{CHBrPh}$ , is easily soluble in alcohol, ether, or glacial acetic acid, but separates from the last solvent in a sparingly soluble modification which crystallises from hot alcohol in white needles and melts and decomposes at  $175^{\circ}$ . C. S.

**4-Acetylamino-2-aminophenol-6-carboxylic Acid.** LEOPOLD CASSELLA & Co. (D.R.-P. 163186).—*p*-Aminosalicylic acid is acetylated, nitrated in sulphuric acid solution, and reduced with iron and acetic acid. The *4-acetylamino-2-aminophenol-6-carboxylic acid* thus obtained crystallises from water in sparingly soluble needles, melts at  $220^{\circ}$ , and forms a sparingly soluble, yellow *diazonium* compound. C. H. D.

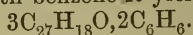
**4-Acetylamino-2-aminophenol-6-sulphonic Acid.** LEOPOLD CASSELLA & Co. (D.R.-P. 163185).—When *p*-acetylaminophenol is dissolved in sulphuric acid at  $95^{\circ}$ , an *o*-sulphonic acid is formed quantitatively. Nitric and sulphuric acids at  $0^{\circ}$  convert it into *2-nitro-4-acetylaminophenol-6-sulphonic acid*, which on reduction yields the *aminosulphonic acid*, separating from water in sparingly soluble, colourless needles and forming readily soluble salts. C. H. D.

**Condensation with Anthranol.** R. PADOVA (*Compt. rend.*, 1906, 143, 121—123).—Anthranol sometimes behaves as if it had the constitution of anthrone,  $\text{H}_2\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO}$ . Experiments have now been made to obtain anthrone derivatives by condensation from anthranol. When heated with benzoyl chloride in pyridine solution, anthranol yields anthraquinone and *benzoylanthranol*, which forms white needles melting at  $163-165^{\circ}$ .

Attempts to condense anthranol with aniline, dimethylaniline, and benzophenone gave no result, but when heated with chlorobenzophenone in xylene solution, hydrogen chloride is evolved, and on cooling crystals separate out, which have been separated by treatment with acetone. The insoluble part consists of dianthranol. From the solution, crystals are obtained which consist of yellow needles melting at  $195-197^{\circ}$  to a ruby-red liquid. This substance is soluble in benzene, xylene, chloroform, acetic acid, pyridine, amyl alcohol, or acetone, slightly so in methyl or ethyl alcohol, and insoluble in light petroleum. All these solutions have a colour ranging from yellow to red. It dissolves in strong sulphuric acid, forming an

emerald-green solution from which water precipitates the substance unchanged. The substance has the composition  $C_{27}H_{18}O$ , and is supposed to be diphenylmethylenanthraquinone,  $CPh_2:C<\overset{C_6H_4}{\underset{C_6H_4}{>}}CO$ .

The molecular weight, determined by the boiling-point method, is normal in ethylene bromide, but the substance is polymerised in benzene and acetone. With benzene it yields a compound,



H. M. D.

**The Fatty Esters of Cholesterol and Phytosterol, and the Anisotropic Liquid Phases of Cholesterol Derivatives.** FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 78—88).—Cholesterol and phytosterol can be easily distinguished crystallographically if the solidification of the fused material is watched on a microscopic slide. The discrete crystals as they separate from a mixture of alcohol and ether are not, on the other hand, easy to distinguish.

A number of esters of cholesterol and phytosterol with the fatty acids were prepared, preferably by boiling the alcohol with the acid anhydride, and their melting points examined. Most of the cholesterol esters examined possessed two liquid phases, namely, an anisotropic and an isotropic liquid phase; with one exception, on the other hand, the phytosterol esters have only one liquid phase. The transition points of the various cholesterol esters have been determined, and a tabular list is given in the paper. The following esters were examined: cholesterol formate, acetate, propionate, butyrate, isobutyrate, valerate, isovalerate, hexoate, octoate, decoate, benzoate, phthalate, and stearate. The formation of the anisotropic liquid was frequently accompanied by a brilliant display of colours; in some cases, namely, the formate, the octoate, and the isovalerate, the anisotropic liquid phase appeared to be labile relatively to the isotropic phase, and could only be obtained by cooling the latter suddenly. Of the phytosterol esters, on the other hand, only the valerate is anomalous, two solid phases appearing to exist, which melt respectively at  $67.1^\circ$  and  $30^\circ$ ; an anisotropic liquid phase appears also to exist.

The melting points of mixtures of cholesterol and phytosterol, and of cholesterol and phytosterol acetates, have been reinvestigated: in both cases the melting point of the substance with the lower melting point, namely, the phytosterol or the cholesterol acetate, is raised by the other constituent of the mixture.

K. J. P. O.

**1:3-Dialkyl Ethers of Pyrogallol.** BASLER CHEMISCHE FABRIK (D.R.-P. 162658).—The trialkyl ethers of pyrogallol or of gallic esters are decomposed when heated with hydroxides of the alkalis or alkaline earths and water under pressure, yielding 1:3-dialkyl ethers of pyrogallol. Thus, the trialkyl gallates decompose according to the equation  $C_6H_2(OR)_3 \cdot CO_2R + 3NaOH = C_6H_2(OR)_2 \cdot ONa + 2R \cdot OH + Na_2CO_3$ .

*Pyrogallol 1:3-dimethyl ether* melts at  $55$ — $56^\circ$  and boils at  $258^\circ$ . The sodium derivative forms large leaflets. *Pyrogallol 1:3-diethyl ether* crystallises from alcohol in long, colourless needles, melts at  $79$ — $80^\circ$ , and boils at  $263$ — $265^\circ$ .

C. H. D.



**Methylenecatechol and Certain of its Derivatives.** EFISIO MAMELI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 101—108).—[With ENRICO BOI.]—Catechol methylene ether, obtained in small yield by Moureu (Abstr., 1897, i, 336) by the interaction of the sodium derivative of catechol and methylene iodide, can be prepared in larger quantity by reducing an alkaline solution of the diazo-chloride of *p*-aminocatechol methylene ether (this vol., i, 93) by means of stannous chloride. When treated with nitric acid of sp. gr. 1.40, catechol methylene ether yields *p*-nitrocatechol methylene ether (compare Jobst and Hesse, Abstr., 1878, 733; 1880, 325), whilst with acid of sp. gr. 1.44—1.52, dinitrocatechol methylene ether (Jobst and Hesse, *loc. cit.*) is obtained.

*p*-Chlorocatechol methylene ether,  $\text{CH}_2 \begin{smallmatrix} \text{O} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \\ \text{O} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \end{smallmatrix} \text{Cl}$ , prepared by the action of cuprous chloride on the diazo-chloride of *p*-aminocatechol methylene ether, is obtained as a colourless oil boiling at 185—187°. It reacts violently with concentrated nitric acid, giving a chloronitro-derivative melting at 128°.

*p*-Bromocatechol methylene ether,  $\text{CH}_2 \text{O}_2 \cdot \text{C}_6\text{H}_3\text{Br}$ , is an oil which has a persistent, pungent odour, boils at 226—228°, dissolves readily in benzene, ether, or light petroleum, and to a less extent in alcohol, reacts energetically with concentrated nitric acid, and gives with concentrated sulphuric acid a carmine-red coloration which rapidly darkens.

*p*-Iodocatechol methylene ether,  $\text{CH}_2 \text{O}_2 \cdot \text{C}_6\text{H}_3\text{I}$ , is obtained as a colourless oil, which boils at 156—157° under 30 mm. pressure and at 257—258° under the ordinary pressure.

T. H. P.

**Derivatives of Dicyanoquinol.** JOHANNES THIELE and FRITZ GÜNTHER (*Annalen*, 1906, 349, 45—66. Compare Abstr., 1900, i, 299).—When an alcoholic solution of chloroquinone and concentrated sulphuric acid is treated with a strong solution of potassium cyanide at the ordinary temperature, a good yield of dicyanoquinol is obtained. The *diacetate*,  $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_2$ , forms white leaflets and melts at 165—166°; the *methyl ether*,  $\text{C}_9\text{H}_6\text{O}_2\text{N}_2 \cdot \text{H}_2\text{O}$ , separates from dilute alcohol in white needles and melts and decomposes at 225°, whilst its *acetate*,  $\text{C}_{11}\text{H}_8\text{O}_3\text{N}_2$ , melts at 136—137°. The dimethyl ether,  $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$ , obtained in a sealed tube at 100° from sodium carbonate, methyl iodide, dicyanoquinol, and a little water, melts at 275°, and forms blue, fluorescent solutions in benzene or glacial acetic acid (compare Kauffmann, this vol., i, 287).

*Dicyano-p-benzoquinone*,  $\text{C}_6\text{H}_2\text{O}_2(\text{CN})_2$ , is obtained by exposing a thin layer of dicyanoquinol in a desiccator to the vapour of concentrated nitric acid under slightly reduced pressure. After purification from chloroform solution, it forms orange-red prisms and melts at 175—180°. Boiling water causes an evolution of hydrogen cyanide and the formation of dicyanoquinol and viscous by-products.

*2:3-Dicyano-6-hydroxyquinol triacetate*,  $\text{C}_{14}\text{H}_{10}\text{O}_6\text{N}_2$ , is obtained by the prolonged action of concentrated sulphuric acid and acetic anhydride on dicyanoquinone. It separates from alcohol in white needles, melts at 160°, and is easily hydrolysed by dilute sulphuric acid to *2:3-dicyano-6-hydroxyquinol*,  $\text{C}_8\text{H}_4\text{O}_3\text{N}_2$ , which decomposes at 250°, gives

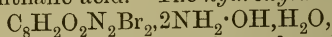
a dark green coloration with ferric chloride, and dissolves in alkalis without fluorescence. *Chlorohydroxyquinol triacetate*,  $C_6H_2Cl(OAc)_3$ , prepared in a similar manner from chlorobenzoquinone, forms white needles and melts at 96—97°.

*Chlorodicyanoquinol*,  $C_8H_3O_2N_2Cl$ , prepared by passing hydrogen chloride into a solution or suspension of dicyanobenzoquinone in chloroform at 0°, forms white needles, melts and decomposes at 190°, develops a violet-red coloration with ferric chloride, and dissolves in sodium carbonate solution with a yellow fluorescence; the *diacetate* melts at 122—123°.

*Chlorodicyanobenzoquinone*,  $C_8HO_2N_2Cl$ , is obtained by oxidising the preceding quinol with the vapour of nitric acid in a desiccator. It separates from chloroform in yellow needles, melts at 154—155° to a dark red liquid, is decomposed by alkalis, and reduced by sulphurous acid. Hydrogen chloride converts it into *dichlorodicyanoquinol*,  $C_8H_2O_2N_2Cl_2$ , which decomposes at 265° and forms a *diacetate* melting at 181—182°.

*Dichlorodicyanobenzoquinone*,  $C_8O_2N_2Cl_2$ , forms golden leaflets, decomposes at 203°, liberates iodine from hydrogen iodide, and is reduced by sulphurous acid. Water decomposes it, producing a red coloration and evolving hydrogen cyanide.

*Dibromodicyanoquinol*,  $C_8H_2O_2N_2Br_2$ , obtained by heating dicyanoquinol in glacial acetic acid with bromine (2 mols.) and potassium acetate (2 mols.), forms yellow leaflets, gives a rose-red coloration with ferric chloride, decomposes at 250°, and cannot be hydrolysed to the corresponding phthalic acid. The *hydroxylamine* salt,



forms yellow needles, decomposes when heated, and is resolved into its components by boiling water. The *diacetate*,  $C_{12}H_6O_4N_2Br_2$ , melts at 199°.

By treatment with acetic anhydride and a few drops of concentrated sulphuric acid, Nef's benzoquinone dibromide (Abstr., 1890, 1272) is slowly changed into 2 : 5-dibromoquinol diacetate.

*Dibromodicyanobenzoquinone*,  $C_8O_2N_2Br_2$ , obtained by oxidising the corresponding quinol with the vapour of nitric acid, crystallises from chloroform in purple-red leaflets, decomposes at 210—217°, and liberates hydrogen cyanide on treatment with water.

The hydrolysis of dicyanoquinol by boiling potassium hydroxide solution gives *p*-dihydroxyphthalic acid,  $C_8H_6O_6$ , in good yield, which separates from water in greenish-yellow needles containing  $\frac{1}{2}H_2O$  and melts at 213° with loss of water. The aqueous solution develops a deep violet coloration with ferric chloride; in alkaline solution a yellow fluorescence is observed. Bromine converts the acid into bromoanil, whilst heating with ammonium carbonate forms a *p*-dihydroxyphthalimide. The *anhydride*,  $C_8H_4O_5$ , obtained at 220—230°, separates from benzene in greenish-yellow nodules, which by exposure to air take up  $1\frac{1}{2}H_2O$  and become sulphur-yellow. The *diacetate* of the anhydride,  $C_{12}H_8O_7$ , separates from benzene and light petroleum in white crystals and melts at 158°.

*p*-*Diacetoxyterephthalic acid*,  $C_{12}H_{10}O_8$ , forms white nodules and is stable at 260°. The *diacetate* of the ethyl ester melts at 156.5°.

*p*-Diacetoxyphtthalimide,  $C_{12}H_8O_6N$ , separates from alcohol in white needles, becomes yellow at  $150^\circ$ , and melts at  $200^\circ$ .

Dichloro-*p*-dihydroxyphtthalimide,  $C_8H_3O_4NCl_2$ , obtained by heating dichlorodicyanoquinol with sulphuric acid and a trace of water, forms greenish-yellow crystals which change colour at  $150^\circ$  but do not melt at  $270^\circ$ .

Dibromo-*p*-dihydroxyphtthalimide,  $C_8H_3O_4NBr_2$ , separates from alcohol as a yellow powder, melts and decomposes at  $250^\circ$ , gives a blue coloration with ferric chloride, and a yellow fluorescence in aqueous-alcoholic solution; the diacetate melts at  $263^\circ$ .

*p*-Dimethoxyphtthalimide, obtained by hydrolysing dicyanoquinol dimethyl ether with concentrated sulphuric acid and a trace of water, forms yellow needles and decomposes at  $200^\circ$ .

*p*-Dimethoxyphtthalic anhydride,  $C_{10}H_8O_5$ , obtained by boiling the preceding compound with alcoholic hydrogen chloride, forms greenish-yellow crystals, melts at  $259^\circ$ , and gives a blue fluorescence in alcoholic acetic acid.

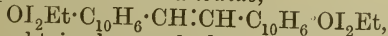
Benzoquinonedicarboxylimide,  $C_6H_2O_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NH}$ , obtained by oxidising *p*-dihydroxyphtthalimide with the vapour of nitric acid, forms brick-red leaflets, decomposes at  $220^\circ$ , and is readily reduced by sulphurous acid. The anhydride,  $C_8H_2O_5$ , prepared in similar manner from *p*-dihydroxyphtthalic anhydride, forms dark red leaflets. C. S.

**Addition of Halogens and of Hydrogen Perhaloids to Oxygen Compounds.** ARTHUR HANTZSCH and OSKAR DENSTORFF (*Annalen*, 1906, 349, 1—44).—The yellow modification of *a*-diethoxydinaphthastilbene (Elbs, Abstr., 1893, i, 271) separates from a concentrated solution in a solvent of high boiling point, and the white form from a dilute solution; if the white needles are removed from the mother liquor, the remaining yellow plates change progressively into the labile modification. The chemical properties of the two modifications are identical, and they behave as physical isomerides. On the contrary, the white and yellow modifications of dibenzoylethylene (Paal, Abstr., 1902, i, 228) are geometrical isomerides, representing the *cis*- and the *trans*-forms respectively.

The additive compounds comprise two classes: (1) perhaloids, compounds of iodine or bromine with organic oxygen compounds, especially those containing an ethereal oxygen atom; (2) hydrogen perhaloids, compounds of  $HBr_n$  and  $HI_n$  with oxygen compounds, especially unsaturated ketones such as dibenzylideneacetone.

In the formation of these substances the nature of the solvent is of the utmost importance. The most suitable are associating solvents, such as benzene, carbon disulphide, and chloroform; dissociating solvents, such as alcohol, pyridine, acetone, or water, are unfavourable.

*a*-Diethoxydinaphthastilbene tetra-iodide,

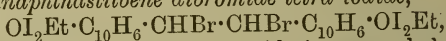


is instantaneously obtained as a dark, voluminous precipitate when a cold solution of diethoxydinaphthastilbene in carbon disulphide, benzene, or chloroform is treated with a large excess of a concentrated



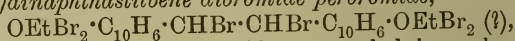
solution of iodine in the same solvent. In the dry state it is an amorphous, dark brown, compact powder, which melts and decomposes at 130—135°. By agitation with excess of carbon disulphide and of decinormal thiosulphate the iodine is removed quantitatively and the organic solvent acquires the pure yellow colour of diethoxydinaphthastilbene. In the freshly-precipitated state, the additive compound dissolves completely when rapidly heated with acetic acid, whereas a month-old preparation is only slightly soluble and decomposes by prolonged boiling.

*a*-Diethoxydinaphthastilbene dibromide tetra-iodide,



is obtained when the colourless dibromide is suspended in benzene and treated with a concentrated solution of iodine in the same solvent. When dry it is reddish-brown, and melts and decomposes at 146—152°.

*a*-Diethoxydinaphthastilbene dibromide perbromide,



is prepared by treating the dibromide, suspended in carbon disulphide at -75°, with a large excess of concentrated bromine solution. The black substance so obtained melts and decomposes at 80—95°, and loses bromine even when dried. Its composition is determined by analogy with the preceding tetraiodide. When the freshly-prepared substance is repeatedly shaken with carbon tetrachloride, glacial acetic acid, and light petroleum in succession, the added halogen is removed and the pure colourless dibromide is regenerated.

When finely-divided diethoxydinaphthastilbene is moistened with glacial acetic acid and treated with a dilute solution of bromine in the same solvent, it is instantly changed into a black substance, which, after being rapidly washed with alcohol and decomposed by alcoholic ammonia, regenerates the diethoxydinaphthastilbene. The substance is too unstable to be analysed, but is regarded as having the composition  $\text{OBr}_2\text{Et}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_{10}\text{H}_6\cdot\text{OBr}_2\text{Et}$ ; at low temperatures it loses bromine, yielding finally almost pure normal diethoxydinaphthastilbene dibromide.

*Dixanthylene tetraiodide*,  $\text{OI}_2\langle\text{C}_6\text{H}_4\rangle\text{C}:\text{C}\langle\text{C}_6\text{H}_4\rangle\text{OI}_2$ , is a black substance which melts and decomposes at 135—140°; it is obtained as a microcrystalline powder by slow separation from the solution. The halogen is removed quantitatively by treatment with alcohol and sodium thiosulphate. In the presence of a large excess of iodine, the tetraiodide absorbs more halogen, yielding an octa- or a deca-iodide.

*Dixanthylene tetrabromide* is a brick-red, flocculent substance which melts and decomposes at 215—220°, and has its halogen removed quantitatively by aqueous-alcoholic sulphurous acid.

Hexane or light petroleum precipitates from a solution of iodine and dimethylpyrone in chloroform or carbon tetrachloride a yellowish-brown, viscous substance which cannot be isolated in a state suitable for analysis, but the existence of an additive compound of the two substances is indicated by the cryoscopic behaviour of their solution in ethylene dibromide, the observed depression being much smaller than the calculated value. The influence of the presence of various foreign substances has been studied, and the results, expressed graphically,

serve to confirm the existence of an additive compound of iodine and dimethylpyrone.

*Bisdimethylpyrone hydrogen tribromide*,  $2O\left\langle\begin{smallmatrix} \text{CMe:CH} \\ \text{CMe:CH} \end{smallmatrix}\right\rangle\text{CO, HBr}_3$ , is formed as an orange, flocculent precipitate on mixing solutions of dimethylpyrone and of bromine in wet ether. The substance is stable for a long time in a desiccator, separates from glacial acetic acid or chloroform in glistening, red needles, melts at  $140\text{--}142^\circ$ , and is insoluble in carbon disulphide, chloroform, or light petroleum. It is decolorised by alcoholic sulphurous acid or alcoholic ammonia, yielding dimethylpyrone.

*Bisdibenzylideneacetone hydrogen pentaiodide*,  $2(\text{CHPh:CH})_2\text{CO, HI}_5$ , is obtained when the calculated quantity of hydrogen iodide, dissolved in benzene, is added to a dilute solution of the two components in an associating solvent. It is a voluminous, brownish-black substance, and melts and decomposes at  $122\text{--}128^\circ$ .

*Bisdianisylideneacetone hydrogen pentaiodide*,  
 $2(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH:CH})_2\text{CO, HI}_5$ ,  
 obtained in a similar manner, is a greyish-black, amorphous substance which melts and decomposes at  $137\text{--}142^\circ$ .

*Bisdianisylideneacetone hydrogen tri-iodide*,  $2\text{C}_{19}\text{H}_{18}\text{O}_3, \text{HI}_3$ , exists in two modifications. One form is obtained by repeatedly extracting the preceding pentaiodide with warm ether, ethyl acetate, or glacial acetic acid until the residue consists of small, glistening, red prisms melting at  $165\text{--}167^\circ$ . When a solution of this form in boiling ethyl acetate or glacial acetic acid is cooled rapidly, the second modification is obtained in the form of dense, greenish-black needles, melting and decomposing at  $156\text{--}159^\circ$ . The latter, which in the mother liquor undergoes partial transformation into the first, can also be obtained by bringing together dianisylideneacetone and iodine in boiling glacial acetic acid or ethyl acetate. Both forms are converted into the penta-iodide by excess of iodine dissolved in benzene; alcohol, on the contrary, removes the halogen and regenerates dianisylideneacetone.

*Bismonoanisylideneacetone hydrogen pentaiodide*,  $2\text{C}_{11}\text{H}_{12}\text{O}_2, \text{HI}_5$ , separates slowly from a warm dilute solution of the ketone and iodine in carbon tetrachloride in the form of bluish-black, glistening leaflets, more quickly on addition of hydrogen iodide dissolved in benzene; it melts and decomposes at  $116\text{--}122^\circ$ . A pure hydrogen tri-iodide has not been obtained. At  $-180^\circ$  the colours of all these compounds become less intense.

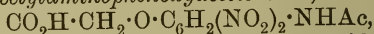
In conformity with the theory that iodine dissolves to a brown solution in those solvents with which it can form additive compounds, the authors find that the intensely brown solution of dimethylpyrone periodide in ethylene dibromide becomes violet by dilution; also at a suitable concentration the brown solution of the same compound in carbon tetrachloride becomes violet by warming, and brown again by cooling.

Dinaphthastilbene and its dibromide do not form additive compounds. This is one of the several arguments advanced by the authors for regarding the halogen or hydrogen perhaloid in the preceding compounds as being united to oxygen by residual affinities.

C. S.

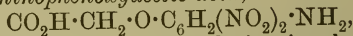
Nitration of *p*-Acetylaminophenoxyacetic Acid, of Diacetyl-*p*-aminophenol, and of *p*-Acetanisidine. FRÉDÉRIC REVERDIN and ARTHUR BUCKY (*Arch. Sci. phys. nat.*, 1906, [iv], 22, 124—145). —As with benzoyl- and dibenzoyl-*p*-aminophenol (Reverdin and Delétra, this vol., i, 165, 273), so also with *p*-acetylaminophenoxyacetic acid, nitration with a mixture of sulphuric and nitric acids yields products different from those obtained by using nitric acid alone (compare Howard, *Abstr.*, 1898, i, 29).

2 : 5-Dinitro-4-acetylaminophenoxyacetic acid,



obtained by the action of sulphuric and nitric acids on *p*-acetylaminophenoxyacetic acid, crystallises in yellow to orange-yellow needles or plates melting at 176°, and dissolves readily in acetic acid, acetone, acetic anhydride, or solutions of the alkali hydroxides or carbonates, to a less extent in alcohol, and only sparingly in benzene or chloroform. Its *barium* salt (+ 2H<sub>2</sub>O) crystallises in small, yellowish-brown prisms slightly soluble in cold water.

2 : 5-Dinitro-4-aminophenoxyacetic acid,



prepared by hydrolysing the acetyl derivative by means of concentrated sulphuric acid, crystallises from water in orange-red needles or plates, melts at 170°, and dissolves readily in alcohol, acetone, acetic acid, or solutions of the alkali hydroxides or carbonates. Its *barium* salt (+ 3H<sub>2</sub>O) separates in brownish-red needles. Its *ethyl* ester crystallises in silky, red needles melting at 144°, and is soluble in acetic acid or benzene. When diazotised and treated with sulphuric acid and potassium iodide, the acid gives (1) an *iodo*-acid, which crystallises from light petroleum in faintly orange, yellow plates, melts at 114—115°, and dissolves in alcohol, benzene, acetic acid, chloroform, or dilute acetone; its *sodium* salt separates in slender, orange needles, its *potassium* salt in red crystals, and its *barium* salt in brown crystals; (2) another *iodo*-acid, crystallising from dilute acetic acid in yellow, flattened needles melting at 201—202°, and dissolving readily in acetone or alcohol and sparingly in benzene or chloroform; its *barium* salt forms yellowish-brown, prismatic needles.

Howard (*loc. cit.*) has assigned an erroneous structure to the acid obtained by the action of nitric acid alone on *p*-acetylaminophenoxyacetic acid, the authors' results showing that 2 : 3-dinitro-4-acetylaminophenoxyacetic acid is obtained under these conditions. The mother liquors from this acid are found to contain another acid, giving, on partial hydrolysis with concentrated sulphuric acid, 3 : 5-dinitro-4-aminophenoxyacetic acid, C<sub>8</sub>H<sub>7</sub>O<sub>7</sub>N<sub>3</sub>, which crystallises from water in long, red needles melting at 190°, and dissolves in alcohol or acetic acid, and to a slight extent in benzene; this acid is decomposed by alcohol, yielding a dinitrophenoxyacetic acid (?), which separates as a pale yellow, crystalline powder melting at 207°.

When diacetyl-*p*-aminophenol is nitrated by means of a mixture of sulphuric and nitric acids, the acetyl derivative of isopicramic acid, melting at 181°, is obtained. In this case, therefore, just as with dibenzoyl-*p*-aminophenol (Reverdin and Dresel, *Abstr.*, 1905, i, 51), one of the acetyl groups first undergoes hydrolysis to hydroxyl. If,



however, a mixture of sulphuric and nitric acids is added to a sulphuric acid solution of diacetyl-*p*-aminophenol containing acetic anhydride, a compound,  $C_7H_6O_6N_3$ , is obtained, which crystallises from dilute alcohol in golden-brown needles, decomposes at  $163.5^\circ$ , and dissolves in water or dilute acetic acid, and to a slight extent in benzene.

The nitroacetylanisidine [ $OMe : NO_2 : NHAc = 1 : 2 : 4$ ] of the Farbwerke vorm. Meister, Lucius, & Brünig (D.R.-P. 101778) crystallises from dilute acetic acid or aqueous alcohol in orange-yellow needles melting at  $148-149^\circ$ , and is soluble in water and slightly so in benzene or light petroleum. When *p*-acetylanisidine is nitrated by means of sulphuric and nitric acids it yields (1) the dinitro-*p*-acetylanisidine melting at  $157^\circ$  (Meldola and Stephens, Trans., 1905, 87, 1199), and (2) a new dinitro-*p*-acetylanisidine [ $OMe : (NO_2)_2 : NHAc = 1 : 2 : 5 : 4$ ], which crystallises from dilute acetic acid in lemon-yellow crystals, melts at  $175.5-176.5^\circ$ , and dissolves readily in acetone, less so in alcohol, and sparingly in water, benzene, or light petroleum. Hydrolysis of the latter compound yields the corresponding dinitro-*p*-anisidine [ $OMe : (NO_2)_2 : NH_2 = 1 : 2 : 5 : 4$ ], which crystallises from a mixture of benzene and light petroleum in red needles melting at  $153^\circ$ , and is soluble in alcohol or acetic acid and readily so in benzene; it does not dissolve in a solution of sodium carbonate, or hydroxide, or ammonia, but gives a violet-red coloration which changes to yellow under the influence of heat.

T. H. P.

**Preparation of Indoxyl and its Homologues.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 163039).—Compounds containing the group  $-NR \cdot CH_2 \cdot CO-$  ( $R = \text{aryl}$ ), such as phenylglycine, phenylglycinephenylglycine, or their homologues, salts, esters, or amides, also phenylhydantoin and diphenylhydantoin, or their homologues, yield derivatives of indoxyl when heated with the alkali or alkaline earth metals or their alloys. The violence of the reaction is moderated by the addition of alkali hydroxides or cyanides.

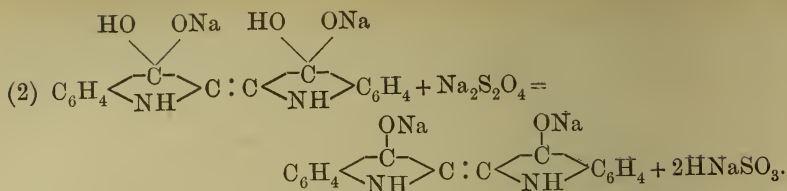
Thus, potassium phenylglycine and an alloy of lead and sodium, added to a fused mixture of potassium and sodium hydroxides, give a product which yields 40–50 per cent. of indigotin on oxidation.

C. H. D.

**Addition of Alkali to Indigotin.** ARTHUR BINZ (*Zeit. angew. Chem.*, 1906, 19, 1415–1418).—When powdered indigo is shaken for several days with alcoholic sodium hydroxide, a dark green powder is obtained which has the composition  $C_{16}H_{10}O_2N_2 \cdot NaOH$ ; on exposure to the air, or on mixing with water, this substance turns blue with liberation of indigotin and sodium hydroxide; if the reaction is carried out at a temperature of  $60^\circ$  it is completed in a few minutes.

The corresponding compound,  $C_{16}H_{10}O_2N_2 \cdot C_6H_5 \cdot ONa$ , which is obtained by heating powdered indigo for some minutes to  $77^\circ$  with alcoholic sodium phenoxide, is a dark green solid. It is assumed accordingly that the reactions taking place in the indigo vat may be represented as follows:





If equation (2) is correct, the reaction should be facilitated by the addition of alcohol, which diminishes hydrolysis. This was shown to be the case by experiment, in which it was found that the reaction took place about thirty times more quickly in alcoholic than in aqueous solution.

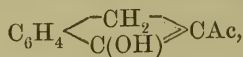
P. H.

**Preparation of the Three Phthalaldehydes.** JOHANNES THIELE and OSKAR GÜNTHER (*Annalen*, 1906, 347, 106—111).—*o*-Phthalaldehyde is prepared by boiling *o*-tetrabromo-*o*-xylene with potassium oxalate and dilute alcohol for forty hours until the whole has dissolved to a pale yellow solution, carbon monoxide and dioxide being evolved. After evaporating the solvent, the aldehyde is distilled in a current of steam and the distillate, after saturation with sodium sulphate, extracted with ethyl acetate. The pure aldehyde, crystallising in yellow needles melting at 56—56.5°, is obtained in a yield of 90 per cent.

[With LEOPOLD.]—*m*-Phthalaldehyde is prepared from *o*-tetrabromo-*m*-xylene,  $\text{C}_6\text{H}_4(\text{CHBr}_2)_2$ , which crystallises in colourless needles melting at 107°. The tetrabromide is converted into corresponding aldehyde in a similar manner to the *o*-derivative; it is purified by conversion into the *trialdehydohydrobenzamide*,  $(\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH})_3\text{N}_2$ , which is a white, insoluble powder. The aldehyde crystallises in colourless needles melting at 89.5°; the dioxime melts at 180°.

K. J. P. O.

**Condensation Products of *o*-Phthalaldehyde.** JOHANNES THIELE and KAUFMAN G. FALK (*Annalen*, 1906, 347, 112—131).—2-Acetyl-3-hydrindone (2-acetyl-3-hydroxyindene),  $\text{C}_6\text{H}_4 \langle \text{CH}_2 \rangle \text{CHAc}$  or



prepared by treating phthalaldehyde and acetone with potassium hydroxide, crystallises in pale yellow needles melting at 76.5°, and is readily soluble in alkali hydroxides; it yields a red coloration with ferric chloride in alcoholic solution, which becomes violet on addition of water. When bromine is added to its alkaline solution, 2:2-dibromohydrindone is obtained. The *phenylhydrazone* of acetylhydrindone crystallises in yellow, flattened needles or leaflets melting at 169—170°, and when treated with hydrochloric acid in methyl-alcoholic solution is converted into a *pyrazole* derivative,  $\text{C}_{17}\text{H}_{14}\text{N}_2$ , which crystallises in colourless prisms and melts at 84°.

*Benzoylhydrindone* (2-benzoyl-3-hydroxyindene),  $\text{C}_6\text{H}_4 \langle \text{CH}_2 \rangle \text{CHBz}$

or  $\text{C}_6\text{H}_4 \langle \text{CH}_2 \rangle \text{C(OH)} \text{CHBz}$ , is prepared in a similar manner from *o*-phthalaldehyde and acetophenone; it crystallises in yellow plates or

pale yellow needles melting at  $98.5^\circ$ , and gives a deep green coloration with ferric chloride; by bromine it is converted into dibromohydrindone. Phenylhydrazine converts it into a corresponding pyrazole,  $C_{22}H_{16}N_2$ , which crystallises in red needles melting at  $174^\circ$ .

The *diphenylhydrazone* of *o*-phthalaldehyde,  $C_6H_4(CH:N_2HPh)_2$ , crystallises in golden-yellow needles melting at  $190-191^\circ$ . When boiled with dilute hydrochloric acid, it is converted into 1-hydroxy-

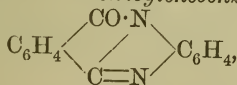
2-phenyl-1:2-dihydrophthalazine,  $C_6H_4 \begin{smallmatrix} \text{CH(OH)·NPh} \\ \text{CH} = \text{N} \end{smallmatrix}$ , which forms

colourless crystals melting at  $128-129^\circ$ ; its *methyl* ether is formed on merely dissolving the compound in methyl alcohol and forms white crystals melting at  $59-60^\circ$ ; the *ethyl* ether melts at  $96-97^\circ$ ; both ethers are reconverted into the original substance by dissolving them in acids and precipitating with an alkali.

*Phenylphthalazonium chloride*,  $C_6H_4 \begin{smallmatrix} \text{CH·NPhCl} \\ \text{CH·N} \end{smallmatrix}$ , is prepared by passing dry hydrogen chloride into a solution of the hydroxydihydrophthalazine or one of its ethers in benzene; it crystallises in white needles melting at  $106-107^\circ$ , and is readily soluble in water. Its *aurichloride* crystallises in yellow needles melting at  $181^\circ$ ; its *platini-chloride* forms orange-red crystals melting at  $224-225^\circ$ .

*Phenylphthalazone*,  $C_6H_4 \begin{smallmatrix} \text{CO·NPh} \\ \text{CH·N} \end{smallmatrix}$ , formed by oxidising the hydroxyphthalazine with alkaline permanganate, crystallises in needles melting at  $106^\circ$ , and is identical with the anhydride obtained by Racine (Abstr., 1887, 951) and Henriques (Abstr., 1888, 842) from phenylhydrazinephthalaldehydic acid.

*o*-Benzylenebenziminazole,  $C_6H_4 \begin{smallmatrix} \text{CH}_2\text{·N} \\ \text{C} = \text{N} \end{smallmatrix} C_6H_4$ , prepared by heating *o*-phthalaldehyde and *o*-phenylenediamine hydrochloride in aqueous solution and then precipitating the base with alkali, crystallises in needles melting at  $210^\circ$ , and yields a *hydrochloride* crystallising in needles; the *sulphate* crystallises in sparingly soluble leaflets; the *platinichloride* forms yellow crystals. When oxidised by permanganate in acid solution, a mixture of *benzoylenebenziminazole*,



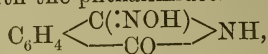
and phenylbenziminazole-*o*-carboxylic acid,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} C_6H_4 \cdot CO_2H$ , is obtained; the former crystallises in yellow needles melting at  $211-212^\circ$ , and when boiled with alkalis or acids is rapidly hydrolysed to the latter, which melts at  $273^\circ$ . It is found to be identical with the "phthalyl-*o*-phenylenediamine" melting at  $266^\circ$ , prepared by Anderlini (Abstr., 1894, i, 375) from phthalic anhydride and *o*-phenylenediamine. The *ethyl* ester,  $C_{16}H_{14}O_2N_2$ , crystallising in leaflets melting at  $163-164^\circ$ , was obtained from the acid prepared by both methods. The *platini-chloride*,  $C_{32}H_{30}O_4N_4 \cdot PtCl_6$ , obtained from the ester, is a yellow pre-



cipitate. When the acid is heated at 280—290°, or treated with acetic anhydride, it is reconverted into benzoylenebenziminazole.

*o*-Tolylenediamine and *o*-phthalaldehyde similarly yield *o*-benzoylene-toliminazole,  $C_6H_4 \begin{array}{c} \text{CH}_2 \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{C} = \text{N} \end{array} C_6H_3\text{Me}$ , which forms colourless crystals melting at 192—193°; the *platinichloride* is a yellow precipitate.

The *compound* obtained by the action of hydroxylamine on *o*-phthalaldehyde is identical with the phthalimideoxime,



prepared by Müller (Abstr., 1886, 802).

K. J. P. O.

**Thio-derivatives of Aromatic Aldehydes and Ketones and their Desulphurisation.** WILHELM MANCHOT and CHR. ZAHN (*Annalen*, 1906, 345, 315—334. Compare Abstr., 1905, i, 342).—*Dithiopiperonaldehyde*,  $C_7H_5O_2 \cdot CH_2 \cdot S \cdot S \cdot CH_2 \cdot C_7H_5O_2$ , results after two to four weeks by the addition of finely-powdered piperonaldehyde to saturated alcoholic ammonium sulphide; it separates from alcohol and acetone in short, white prisms, melts at 69·5°, gives a carmine-red coloration with concentrated sulphuric acid, and is reduced by zinc dust and glacial acetic acid to the *mercaptan*,  $C_8H_7O_2 \cdot SH$ , a yellow oil which forms yellow *lead* and *copper* salts, a greenish-yellow *silver* salt, and is reconverted into the disulphide by alcoholic iodine.

*Dithiopiperonaldehyde hydrosulphide*,  $C_{16}H_{14}O_4S_2 \cdot H_2S$ , results when alcoholic ammonium sulphide containing excess of hydrogen sulphide is used, and the mixture shaken for many days; it crystallises in slender needles, melts at 113°, does not form mercury or lead salts, is reduced to the mercaptan, and readily loses sulphur by treatment with a solution of sodium ethoxide or with copper powder.

[*Bis*:3:4-methylenedioxydibenzyl],  $C_{16}H_{14}O_4$ , obtained from the disulphide and copper powder at 280° or by prolonged boiling in xylene, separates from alcohol in slender needles, melts at 138°, and yields a *bromide*,  $C_{16}H_{12}O_4Br_2$ , which melts at 164°.

*Dithiovanillin*,  $C_{16}H_{18}O_4S_2$ , obtained in a similar manner to the preceding disulphide, melts at 129—130°, loses sulphur by treatment with concentrated sulphuric acid or sodium hydroxide, and hydrogen sulphide by treatment with zinc dust and acetic acid; the *benzoyl* derivative,  $C_{30}H_{26}O_6S_2$ , melts at 133—135°, and does not form mercury or lead salts. *Dithiobromovanillin*,  $C_{16}H_{16}O_4Br_2S_2$ , prepared from Tie-mann's bromovanillin, melts at 159°.

4:4'-*Dihydroxy*:3:3'-*dimethoxydibenzyl*,  $C_{16}H_{18}O_4$ , obtained from copper powder and dithiovanillin by heating alone or in xylene solution, forms long, slender needles, melts at 158°, produces a mirror with ammoniacal silver solutions, and yields a *bromide*,  $C_{16}H_{14}O_4Br_4$ , which melts at 214°.

Dithioanisaldehyde,  $C_{16}H_{18}O_2S_2$ , prepared previously in an impure state by Baumann and Fromm (Abstr., 1891, 1050), melts at 101°, and by careful heating with copper powder, alone or in xylene solution, yields [*p*-bismethoxydibenzyl],  $OMe \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot OMe$ , which separates from alcohol in large needles, develops a magnificent red

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coloration with ferric chloride and concentrated sulphuric acid, and yields a *bromide*,  $C_{16}H_{16}O_2Br_2$ , which melts at  $147^\circ$ .

[By G. KRÄNZLEIN.]—*Dithio-p-dimethylaminobenzaldehyde*,  $C_{18}H_{24}N_2S_2$ , prepared like the preceding disulphides or by heating *p*-dimethylaminobenzaldehyde and ammonium sulphide at  $100$ – $120^\circ$ , separates from alcohol in elongated prisms, melts at  $83.5^\circ$ , yields the *mercaptan* by reduction with sodium amalgam, and forms a *hydrochloride*,

which melts at  $211^\circ$ .  $C_{18}H_{24}N_2S_2 \cdot 2HCl$ , *Bis-p-dimethylaminodibenzyl*,  $C_{18}H_{24}N_2$ , boils at  $105^\circ$  under 25 mm. pressure, and forms a *platinichloride*,

$C_{18}H_{24}N_2 \cdot H_2PtCl_6$ . *See entry 1,902 p. 1266*

When *p*-dimethylaminobenzaldehyde is treated with alcoholic ammonium sulphide containing excess of hydrogen sulphide, a *hydro-sulphide*,  $C_{18}H_{24}N_2S_2 \cdot H_2S$ , is obtained, which melts at  $162^\circ$ .

[*Bis-3:4-methylenedioxy stilbene*,]  $C_7H_5O_2 \cdot CH:CH \cdot C_7H_5O_2$ , obtained by heating  $\alpha$ -trithiopiperonaldehyde (Wörner, Abstr., 1896, i, 225) and copper above  $200^\circ$ , separates from glacial acetic acid in short prisms and melts at  $206^\circ$ .  
C. S.

**Reaction between Unsaturated Compounds and Organic Magnesium Compounds. IX. Reactions with Stereoisomerides.** ELMER P. KOHLER (*Amer. Chem. J.*, 1906, 36, 177–195. Compare this vol., i, 427; Kipping and Salway, *Trans.*, 1904, 85, 438).—The action of magnesium ethyl bromide on benzylidenedeoxybenzoin and *isobenzylidenedeoxybenzoin*, and treatment of the product with water or hydrochloric acid cooled with ice, leads to the formation of the two forms of  $\alpha\beta$ -diphenylvalerophenone, the relative amounts of the isomerides contained varying with the method of isolation. The action of benzoyl chloride on the magnesium compounds from the two isomerides results in the formation of the same  $\alpha\beta\gamma$ -triphenyl- $\Delta^a$ -pentenyl benzoate,  $CH_3EtPh \cdot CPh: CPh \cdot O \cdot CPh$ , which crystallises from alcohol in long needles, melts at  $143^\circ$ , is not changed by heating at  $150^\circ$  for forty hours or by exposure to sunlight in benzene iodine solution, and on hydrolysis with aqueous potassium hydroxide cooled by ice or with concentrated hydrochloric acid at  $150^\circ$  yields the  $\alpha\beta$ -diphenylvalerophenone melting at  $170^\circ$ . The product obtained on hydrolysis of the benzoate with boiling alcoholic hydrogen chloride contains 10 per cent., or, with cold alcoholic hydrogen chloride, 14 per cent., of the isomeric ketone melting at  $92^\circ$ . The ketone melting at  $92^\circ$  is converted rapidly by potassium hydroxide, more slowly by hydrochloric acid, into its isomeride melting at  $170^\circ$ .

$\alpha\beta\gamma$ -Triphenyl- $\Delta^a$ -pentenyl acetate,  $CH_3EtPh \cdot CPh: CPh \cdot OAc$ , formed in a similar manner to the benzoate, crystallises in slender needles, melts at  $120^\circ$ , and on hydrolysis behaves in the same manner as the benzoate.

If the additive compound of magnesium ethyl bromide and benzylidene- or *isobenzylidenedeoxybenzoin* is poured on to ice and ether free from alcohol, it yields an oil which is probably  $\alpha\beta\gamma$ -triphenyl- $\Delta^a$ -pentenol,  $CH_3EtPh \cdot CPh: CPh \cdot OH$ ; this is readily soluble in cold light petroleum, reduces potassium permanganate in acetone solution, and in

a freezing mixture changes slowly into  $\alpha\beta$ -diphenylvalerophenone, of which 99.62 per cent. melts at  $92^\circ$  and 0.38 per cent. at  $170^\circ$ . When a current of air is passed through the moist ethereal solution of the enol cooled by a freezing mixture, the *peroxide*,  $\text{CHEtPh} \cdot \text{CPh} < \begin{smallmatrix} \text{O}_2 \\ | \\ \text{CPh} \cdot \text{OH} \end{smallmatrix}$ ,

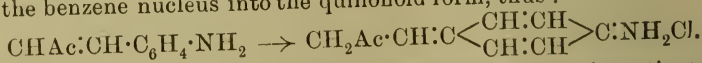
is formed in two modifications, one of which crystallises from acetone in stout needles and melts at  $166^\circ$ ; the other crystallises in large, transparent prisms and melts at  $109^\circ$ . These peroxides are not formed by the action of air or oxygen on  $\alpha\beta$ -diphenylvalerophenone; they are stable, do not yield hydrogen peroxide with water, do not liberate iodine from iodides, do not oxidise indigo, when heated in quantity decompose with a flash but without detonation, forming benzoic acid and ethyldeoxybenzoin, and react with magnesium ethyl bromide forming a *product* from which the peroxides are again formed on treatment with ice.

$\alpha\beta\gamma\gamma$ -Tetraphenyl- $\Delta^a$ -propenol,  $\text{CHPh}_2 \cdot \text{CPh} \cdot \text{CPh} \cdot \text{OH}$ , prepared by the action of magnesium phenyl bromide on benzylidenedeoxybenzoin in light petroleum solution, and treatment of the product with ice and ether free from alcohol, separates from light petroleum in colourless needles, melts at about  $95$ – $100^\circ$ , and changes into triphenylpropionophenone when slowly heated below its melting point. The *peroxide*,

$\text{CHPh}_2 \cdot \text{CPh} < \begin{smallmatrix} \text{O}_2 \\ | \\ \text{CPh} \cdot \text{OH} \end{smallmatrix}$ , crystallises in small, lustrous prisms, melts at  $127^\circ$ , and when heated alone, or with hydrochloric acid in alcoholic solution, decomposes, forming benzoic acid and diphenylacetophenone (Delacre, Abstr., 1896, i, 486; Biltz, Abstr., 1899, i, 439); this forms an *additive* compound with magnesium ethyl bromide, which reacts with water, yielding the *alcohol*,  $\text{CHPh}_2 \cdot \text{CEtPh} \cdot \text{OH}$ , crystallising in needles and melting at  $91^\circ$ . The *oxime* of diphenylacetophenone,  $\text{CHPh}_2 \cdot \text{CPh} \cdot \text{NOH}$ , is obtained in small yields by the action of hydroxylamine hydrochloride on the ketone in aqueous potassium hydroxide solution. It crystallises from acetone in plates and melts at  $182^\circ$ .

*Bromotriphenylpropionophenone*,  $\text{CHPh}_2 \cdot \text{CBrPh} \cdot \text{COPh}$ , prepared by treating the magnesium derivative of tetraphenylpropenol with bromine, crystallises in large prisms, melts at  $124^\circ$ , and readily loses hydrogen bromide. G. Y.

**Methinammonium Compounds.** HANS RUPE and A. PORAI-KOSCHITZ (*Zeit. Farb. Ind.*, 1906, 5, 317–321).—The coloured salts of *p*-aminobenzylideneacetone are thought to be produced by a transition of the benzene nucleus into the quinonoid form, thus:



In order to test this hypothesis, it was necessary to investigate the *m*-amino-compounds. Since the acetone derivatives are difficult to prepare, the corresponding acetophenone derivatives have been studied.

*m*-Aminobenzylideneacetophenone,  $[\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{COPh}]$ , prepared by reducing the corresponding nitro-derivative with stannous chloride in acetic acid solution, crystallises in pale yellowish-green, rhombic leaflets melting at  $159^\circ$ ; it dissolves in hydrochloric acid, forming

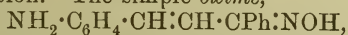
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a completely colourless solution, from which the *hydrochloride* can be isolated as colourless needles. The *sulphate* is similar. The *acetyl* derivative, prepared from the hydrochloride and acetic anhydride in the presence of sodium acetate, crystallises in yellow, prismatic needles melting at  $104^{\circ}$ .

*p*-Aminobenzylideneacetophenone crystallises in golden leaflets melting at  $151^{\circ}$ ; it dissolves in moderately dilute hydrochloric acid, forming a deep red solution, which becomes decolorised by addition of concentrated hydrochloric acid, flesh-coloured needles finally separating. These crystals dissolve in hot concentrated hydrochloric acid with a red coloration, which, however, disappears on cooling. If water is cautiously added to the red solution, red crystals separate. Both forms have the same composition,  $C_{15}H_{13}ON, HCl$ . The solution of the base in acetic acid is deep red, and deposits dark red leaflets, which, on slowly heating, fade in colour, and finally melt at  $151^{\circ}$ , the melting point of the base. The *acetyl* derivative crystallises in pale green leaflets melting at  $179^{\circ}$ .

*p*-Aminoacetophenone and hydroxylamine yield two compounds according as sodium hydroxide or carbonate has been used to bring about the condensation. The simple *oxime*,

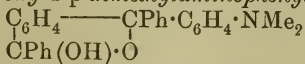


is formed in the presence of the hydroxide, and crystallises in leaflets melting at  $139^{\circ}$ . In presence of sodium carbonate, an *oximido-oxime*,  $NH_2 \cdot C_6H_4 \cdot CH(NH \cdot OH) \cdot CH_2 \cdot CPh:NOH$ , is produced, and crystallises in needles melting at  $178.5-179^{\circ}$ ; the *hydrochloride* is sparingly soluble.

*p*-Dimethylaminobenzylideneacetophenone forms a bluish-grey hydrochloride when treated with a small quantity of fuming hydrochloric acid; the solution in hydrochloric acid is blue. The base dissolves in dilute hot hydrochloric acid with a deep red coloration, which disappears on cooling, the solution depositing a colourless, crystalline *hydrochloride*,  $C_{17}H_{17}ON, HCl$ , crystallising in needles; this material again dissolves in hot acid with a red coloration. In concentrated sulphuric acid, the base forms a colourless solution, from which a small quantity of water precipitates a colourless sulphate. The solution in hot acid is red. The *phenylhydrazone* of *p*-dimethylaminobenzylideneacetophenone,  $NMe_2 \cdot C_6H_4 \cdot CH:CH \cdot CPh:N \cdot NHPh$ , forms very pale green needles melting at  $127-128^{\circ}$ .

K. J. P. O.

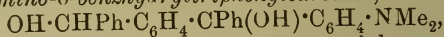
**Action of Magnesium Phenyl Bromide on Dialkylaminobenzoylbenzoic Esters.** J. PÉCARD (*Compt. rend.*, 1906, 143, 237—239).—2-Hydroxy-1-*p*-dimethylaminophenyl-1:2-diphenyl-1:2-dihydroisobenzofuran,



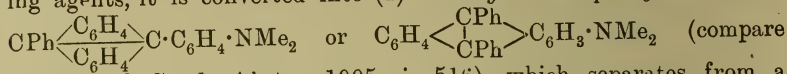
prepared by the action of excess of magnesium phenyl bromide on methyl dimethylaminobenzoylbenzoate (Haller and Guyot, *Abstr.*, 1904, i, 602), crystallises from a mixture of benzene and alcohol in slender, faintly yellow needles melting at  $194^{\circ}$  (uncorr.), and dissolves in the hydrocarbons, to a less extent in the alcohols, and sparingly in ether or acetone. It is soluble in acids, forming intensely red salts, which crystallise from acetone in slender needles and are dissociated by water. The *picrate*

melts and decomposes at  $246^{\circ}$ . The *methyl* and *ethyl* ethers crystallise from a mixture of benzene and alcohol in colourless prisms and melt at  $158^{\circ}$  and  $169^{\circ}$  respectively.

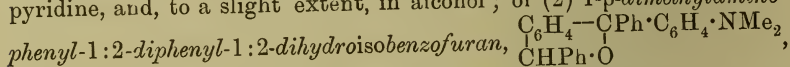
*p*-Dimethylamino-*o*-benzhydryltriphenylcarbinol,



prepared by reducing the preceding compound by means of sodium amalgam and alcohol, separates from a mixture of alcohol and ether in white crystals and melts at  $145^{\circ}$ . Under the action of dehydrating agents, it is converted into (1) *dimethylaminodiphenylanthracene*,



Guyot and Catel, *Abstr.*, 1905, i, 516), which separates from a mixture of benzene and light petroleum in microscopic, green crystals melting at  $298^{\circ}$ , and dissolves in acetic acid, carbon disulphide, or pyridine, and, to a slight extent, in alcohol; or (2) 1-*p*-dimethylamino-



which crystallises from a mixture of benzene and alcohol in white prisms melting at  $110^{\circ}$ .  
T. H. P.

**Introduction of Dinaphthapyryl and Xanthyl Radicles into Electro-negative Molecules.** ROBERT FOSSE and A. ROBYN (*Compt. rend.*, 1906, 143, 239—242).—Dinaphthapyryl and xanthyl radicles can readily be substituted for a hydrogen atom of various electro-negative organic molecules, such as  $\beta$ -ketonic esters,  $\beta$ -diketones, or ethyl malonate or cyanoacetate, by: (1) the action of heat on a molecular mixture of xanthidrol with a  $\beta$ -ketonic or cyanoacetic ester; (2) contact in an acetic acid medium of either xanthidrol and a  $\beta$ -ketone or dinaphthapyranol and an acetoacetic ester; (3) double decomposition between dinaphthapyryl bromide and the sodium derivative of a  $\beta$ -ketonic ester, a  $\beta$ -diketone, or a malonic or cyanoacetic ester.

It has not been determined whether the union of the two constituent radicles of the compounds thus obtained is by means of carbon-carbon, carbon-oxygen, or oxygen-oxygen.

The following new compounds have been prepared:

*Ethyl xanthylacetoacetate*,  $\left[ \text{O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CH} \right] [\text{CHAc} \cdot \text{CO}_2\text{Et}]$ , forms white, nacreous crystals and melts at  $87$ — $89^{\circ}$ .

*Ethyl xanthylethylacetoacetate*,  $\left[ \text{O}(\text{C}_6\text{H}_4)_2\text{CH} \right] [\text{CEtAc} \cdot \text{CO}_2\text{Et}]$ , prepared by the action of sodium and ethyl iodide on the preceding compound, forms plates melting at  $126$ — $127^{\circ}$ .

*Ethyl xanthylbenzoylacetoacetate*,  $\left[ \text{O}(\text{C}_6\text{H}_4)_2\text{CH} \right] [\text{CHBz} \cdot \text{CO}_2\text{Et}]$ , forms groups of white needles melting at  $80^{\circ}$ .

*Dinaphthapyrylacetylacetone*,  $\left[ \text{O} \begin{array}{c} \text{C}_{10}\text{H}_6 \\ \diagup \quad \diagdown \\ \text{C}_{10}\text{H}_6 \end{array} \text{CH} \right] [\text{CHAc}_2]$ , forms colourless crystals melting at  $155$ — $157^{\circ}$  (uncorr.).

*Xanthylacetylacetone*,  $\left[ \text{O}(\text{C}_6\text{H}_4)_2\text{CH} \right] [\text{CHAc}_2]$ , crystallises in long, white needles melting at  $141$ — $142^{\circ}$  (uncorr.).

*Dinaphthapyrylbenzoylacetoacetone*,  $\left[ \text{O}(\text{C}_{10}\text{H}_6)_2\text{CH} \right] [\text{CHAcBz}]$ , forms colourless crystals melting and decomposing at about  $201$ — $204^{\circ}$ .

*Xanthylbenzoylacetone*,  $[\text{O}(\text{C}_6\text{H}_4)_2\text{CH}][\text{CHAcBz}]$ , forms white crystals melting at  $171^\circ$  (uncorr.).

*Ethyl dinaphthapyrylmalonate*,  $[\text{O}(\text{C}_{10}\text{H}_6)_2\text{CH}][\text{CH}(\text{CO}_2\text{Et})_2]$ , forms large, colourless crystals melting at  $109\text{--}110^\circ$ .

*Ethyl dinaphthapyrylcyanoacetate*,  $[\text{O}(\text{C}_{10}\text{H}_6)_2\text{CH}][\text{CN}\cdot\text{CH}\cdot\text{CO}_2\text{Et}]$ , melts at  $158\text{--}159^\circ$  (uncorr.).

*Ethyl xanthylcyanoacetate*,  $[\text{O}(\text{C}_6\text{H}_4)_2\text{CH}][\text{CN}\cdot\text{CH}\cdot\text{CO}_2\text{Et}]$ , forms pale green crystals melting at  $124\text{--}126^\circ$  (uncorr.). T. H. P.

**Grignard's Reaction.** RICHARD MEYER and KARL TÖGEL (*Annalen*, 1906, 347, 55—92).—The use of Grignard's reaction in the synthesis of benzoic acid has been studied (compare Houben and Kesselkaul, Abstr., 1902, i, 583; and Zelinsky, *ibid.*, 675). The action of carbon dioxide on magnesium phenyl bromide was mainly used, a trace of iodine being added as an accelerator. The influence of moisture and of temperature on the products of the reaction were studied in detail.

When magnesium is added to an ethereal solution of bromobenzene and carbon dioxide slowly passed in, benzoic acid is produced in nearly a theoretical yield, if the presence of moisture is most carefully avoided. At the same time a trace of diphenyl is always formed.

In the presence of even an extremely small quantity of water the yield of benzoic acid falls to 25 per cent., whilst that of the diphenyl rises to about 65 per cent.

If the water is introduced not at the beginning but towards the end of the reaction, a third product, benzene, is formed at the expense of the benzoic acid and the diphenyl. The percentage of benzene is in the most favourable circumstances 64, whereas that of the benzoic acid is now 20, and that of the diphenyl 45.

At temperatures above  $0^\circ$  other products are formed; of these the chief is triphenylcarbinol, an oil being produced at the same time from which, on fractionation under reduced pressure, benzophenone and triphenylmethane can be isolated in small quantity together with diphenyl- and triphenyl-carbinols (compare Schroeter, Abstr., 1903, i, 821). In all the reactions above mentioned a trace of phenol is formed.

It is suggested that the following series of reactions takes place. In the absence of water the main reaction is represented by the equations:  $\text{C}_6\text{H}_5\text{Br} + \text{Mg} = \text{C}_6\text{H}_5\cdot\text{MgBr}$ ;  $\text{C}_6\text{H}_5\cdot\text{MgBr} + \text{CO}_2 = \text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{MgBr}$ . The diphenyl is formed probably according to the equation:  $2\text{C}_6\text{H}_5\text{Br} + \text{Mg} = \text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5 + \text{MgBr}_2$ , but it is probably also produced as the result of other changes in which phenol is the first product:  $\text{C}_6\text{H}_5\cdot\text{MgBr} + \text{H}_2\text{O} + \text{O} = \text{C}_6\text{H}_5\cdot\text{OH} + \text{MgBr}\cdot\text{OH}$ ;  $\text{C}_6\text{H}_5\cdot\text{MgBr} + \text{C}_6\text{H}_5\cdot\text{OH} = \text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5 + \text{MgBr}\cdot\text{OH}$ . Hence only traces of phenol can be detected. In a special experiment, in which freshly-prepared magnesium phenyl bromide was treated with one mol. of phenol, rather more than one mol. of diphenyl was formed; prepared in this way, however, this substance could not be purified readily.

The benzene is most probably the result of the simple action of water on magnesium phenyl bromide:  $\text{C}_6\text{H}_5\cdot\text{MgBr} + \text{H}_2\text{O} = \text{C}_6\text{H}_6 + \text{MgBr}\cdot\text{OH}$ , a result which was tested by treating magnesium phenyl



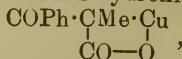
bromide with carbon dioxide in the presence of varying quantities of water. The benzophenone results from the interaction of one mol. of carbon dioxide with two mols. of magnesium phenyl bromide and subsequent decomposition of the additive product with water. The triphenylcarbinol is probably not produced directly from carbon dioxide and magnesium phenyl bromide, but from benzophenone, thus:  $\text{COPh}_2 + \text{C}_6\text{H}_5 \cdot \text{MgBr} = \text{CPh}_3 \cdot \text{O} \cdot \text{MgBr} \rightarrow \text{CPh}_3 \cdot \text{OH}$ , in harmony with the production of tertiary alcohols from ketones by Grignard's reaction. The triphenylmethane is probably a reduction product of the forerunner of the triphenylcarbinol.

*Synthesis of the Esters of Ketonic Acids.*—Unsuccessful attempts have been made to synthesise the esters of ketonic acids by the action of magnesium on a mixture of molecular proportions of an acyl chloride and halogenated ester. A magnesium-gold couple and a mercury-aluminium couple were also tried and found to be useless; but Grignard's reagent in the presence of a trace of aluminium can be used successfully if the right concentrations of ether are chosen. It is of importance to allow the magnesium to interact first with the halogenated ester.

Ethyl benzoylacetate is prepared by adding magnesium ribbon to a solution of ethyl bromoacetate in ether containing a trace of iodine. A vigorous reaction takes place as the magnesium dissolves and a thick oil separates; benzoyl bromide is now added in small portions and the mixture heated. The ethyl benzoylacetate is then converted into the sodium derivative and after acidification extracted with ether.

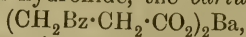
Benzoylacetic acid is obtained from the ester by hydrolysing by Ceresole's method; the acid melts and decomposes at  $100-101^\circ$ . Ethyl benzoylacetate was also prepared, but with a less satisfactory yield, from ethyl chloroacetate and benzoyl chloride in the presence of aluminium and magnesium.

*Ethyl  $\alpha$ -benzoylpropionate*, similarly prepared from ethyl  $\alpha$ -bromopropionate and benzoyl bromide, boils at  $100-102^\circ$  under 48 mm. pressure. The *copper* salt is a green powder decomposing at  $180^\circ$  and readily soluble in organic solvents. If the ester is treated with copper acetate in the presence of an alkali hydroxide, the *copper* salt,



is produced. Attempts to obtain  $\alpha$ -dibenzoylpropionic acid and tribenzoylacetic acid led to no results. When ethyl  $\alpha$ -benzoylpropionate is hydrolysed, only benzoic and propionic acids are isolated.

*Ethyl  $\beta$ -benzoylpropionate*, obtained by the method above described from ethyl  $\beta$ -iodopropionate and benzoyl bromide, crystallises in leaflets, melts at  $19^\circ$ , and boils at  $183-184^\circ$  under 22 mm. pressure. When hydrolysed with barium hydroxide, the *barium* salt,



is obtained and crystallises in small needles. From the latter, the acid can be easily prepared.  $\beta$ -Dibenzoylpropionic acid, obtained by the action of benzoyl chloride on ethyl  $\beta$ -benzoylpropionate in the presence of sodium ethoxide, melts at  $194^\circ$  and gives a red coloration with ferric chloride.

Ethyl acetoacetate is prepared from ethyl bromoacetate and acetyl chloride.

Attempts to condense ethyl *m*-bromobenzoate with benzoyl bromide failed. K. J. P. O.

**Pechmann's Dye [from Benzoylacrylic Acid].** I. TAD. KÓZ-NIEWSKI and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1906, 81—95).—Homologues of benzoylacrylic acid have been prepared by condensing aromatic hydrocarbons with maleic anhydride in the presence of aluminium chloride. The *phenylhydrazone* of benzoylacrylic acid,  $C_{16}H_{14}O_2N_2$ , crystallises from benzene in golden-yellow needles and melts at  $197^\circ$ . The *methyl ester* of the acid,  $COPh \cdot CH:CH \cdot CO_2Me$ , forms pale yellow needles melting at  $30-32^\circ$ , and boiling at  $185^\circ$  under 16 mm. pressure.

*m*-Xyloylacrylic acid,  $C_6H_3Me_2 \cdot CO \cdot CH:CH \cdot CO_2H$ , is best prepared at low temperatures, and melts at  $114^\circ$ . Phenetoylacrylic acid,  $OEt \cdot C_6H_4 \cdot CO \cdot CH:CH \cdot CO_2H$ , melts at  $143-144^\circ$ ;  $\psi$ -cumoylacrylic acid,  $C_6H_2Me_3 \cdot CO \cdot CH:CH \cdot CO_2H$ , melts at  $149^\circ$ , and the isomeric mesitoylacrylic acid at  $140.5^\circ$ .

Each acid yields a dye corresponding with Pechmann's dye from benzoylacrylic acid (Abstr., 1882, 1074) when warmed with dehydrating agents, especially acetic anhydride. The yields in most cases are poor. A better yield of dye appears to be formed when the benzoylacrylic acid contains  $\gamma$ -keto- $\alpha$ -hydroxyphenylbutyric acid, due to admixture of malic anhydride with the maleic anhydride. The dye from mesitoylacrylic acid is more readily soluble in chloroform or xylene than its homologues, and its solutions are coloured reddish-yellow, and possess a somewhat different absorption spectrum.

When oxidised, the dye from benzoylacrylic acid yields benzoic, and that from toluylacrylic acid, terephthalic acid. The dye from benzoylacrylic acid reacts with aniline and acetic acid, yielding a *dianilide*,  $C_{32}H_{22}O_2N_2$ , which crystallises in dark green, glistening needles soluble in xylene to a deep purple solution. Both alcoholic potassium hydroxide and bromine react with Pechmann's dye, for which the formula  $COPh \cdot C \begin{smallmatrix} \diagup CO \cdot CH \\ \diagdown CH \cdot CO \end{smallmatrix} C \cdot COPh$  is suggested. J. J. S.

**Hippocoprosterol.** GERSON GITTELMACHER-WILENKO (*Bull. Acad. Sci. Cracow*, 1906, 20—23).—Bondzyński and Humnicki's hippocoprosterol (Abstr., 1897, i, 183) consists of two compounds.

$\alpha$ -Hippocoprosterol,  $C_{27}H_{54}O$  or  $C_{27}H_{52}O$ , dissolves readily in 97 per cent. alcohol, crystallises in slender, rhombic plates resembling cholesterol, and melts at  $66-67^\circ$ . It gives Salkowski's and Liebermann's reactions but feebly.

$\beta$ -Hippocoprosterol,  $C_{27}H_{52}O$  or  $C_{27}H_{50}O$ , is almost insoluble in cold alcohol, separates as a gelatinous mass of minute needles, and melts at  $56^\circ$ . J. J. S.

**$\beta$ -Nitroisoapioles.** ENRICO RIMINI and F. OLIVARI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 138—141).—Dill *isoapiole nitrosite*,  $C_{12}H_{14}O_7N_2$ , prepared by a method analogous to that used for obtaining isomyristicin

nitrosite (compare Rimini, Abstr., 1905, i, 656), is a lemon-yellow powder melting and decomposing at about  $134^{\circ}$ . The corresponding  $\beta$ -nitroisoapiole,  $C_{12}H_{13}O_6N$ , separates from alcohol in yellow crystals and melts at  $94-95^{\circ}$ .

The isomeric  $\beta$ -nitroisoapiole, obtained from parsley oil, crystallises from alcohol in silky, yellow needles melting at  $96^{\circ}$ . The bromo-derivative,  $C_6Br(O_2CH_2)(OMe)_2 \cdot CH: CMe \cdot NO_2$ , crystallises from alcohol in yellow laminae melting at  $120^{\circ}$ . On treatment with hydroxylamine (1 mol.), this  $\beta$ -nitroisoapiole, in aqueous-alcoholic solution, gives apiolaldoxime,  $C_{11}H_{10}O_5N$ , melting at  $160^{\circ}$ .

In the preparation of  $\beta$ -nitroisomyristicin (*loc. cit.*), myristicinaldehyde is also formed, and in that of  $\beta$ -nitroisoapiole from parsley oil, apiolaldehyde is obtained in small quantity. T. H. P.

**Bixin.** The Colouring Matter of Bixa Orleana. I. LEON MARCHLEWSKI and LAD. MATEJKO (*Bull. Acad. Sci. Cracow*, 1905, 745—753. Compare Etti, *Ber.*, 1878, 11, 864; Zwick, Abstr., 1897, i, 630).—Bixin crystallises from a mixture of chloroform and alcohol or from glacial acetic acid in dark red rhomboids melting at  $198^{\circ}$  when heated quickly, or at  $191.5^{\circ}$  when slowly heated. Its solubility in chloroform at  $25^{\circ}$  is 0.34 gram per 100. The analyses agree with Etti's formula,  $C_{28}H_{34}O_5$ . Its spectra in chloroform and alcoholic solutions are similar to those of lipochrom (*Proc. Roy. Soc.*, 1898, 63, 389; 1899, 65, 177). Monosodium and potassium salts have been prepared. Bixin contains one methoxyl group, and although it possesses distinct acidic properties, definite alkyl derivatives could not be prepared. When reduced with zinc dust and acetic acid, bixin yields an orange product melting at  $200.5^{\circ}$ . It rapidly changes when exposed to the air at  $100^{\circ}$  and becomes colourless. J. J. S.

**Tannins.** II. Eutannin. HERMANN THOMS (*Chem. Centr.*, 1906, i, 1829—1830; from *Apoth.-Zeit.*, 21, 354—356. Compare this vol., ii, 504).—Commercial eutannin, free from lactose, is found to be identical with chebulinic acid,  $C_{28}H_{22}O_{19}$ . It crystallises from water in small, colourless needles containing  $H_2O$  and decomposing at  $234^{\circ}$ , and dissolves readily in alcohol, acetone, ethyl acetate, or amyl alcohol, sparingly in chloroform or light petroleum. It reacts acid towards litmus and has  $[\alpha]_D$  initially  $+61.7^{\circ}$ , gradually rising to  $+66.9^{\circ}$ . It forms an *ennea-acetyl* derivative and a *methyl* derivative, the latter yielding trimethylgallic acid when treated with concentrated sodium hydroxide solution. When heated with water at  $100-150^{\circ}$ , eutannin yields gallic acid and *eutannin hydrate*,  $C_{28}H_{24}O_{20}$ , which is a white, amorphous powder decomposing at  $200-210^{\circ}$ ; it dissolves readily in water, alcohol, acetone, or ethyl acetate and moderately in ether.

On dissolving eutannin in cold dilute sodium hydroxide solution in absence of air and subsequently acidifying with acetic acid and adding lead acetate solution, a precipitate is formed which, when treated with hydrogen sulphide, yields gallic acid and a *decomposition-tannin*,  $C_{14}H_{16}O_{12}$  or  $C_{14}H_{14}O_{11}$ , as a pale yellow, amorphous powder, soluble in water, alcohol, acetone, ethyl acetate, or ether; it decomposes at about  $260^{\circ}$ , has  $[\alpha]_D +26^{\circ}$  at  $15^{\circ}$ , gives a blue coloration with ferric chloride,



reduces Fehling's solution slightly, has an acid reaction towards litmus, and yields a white precipitate with quinine salts.

Probable formulæ are suggested for the above compounds.

T. H. P.

**Quebracho Tannin.** II. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 1893; from *Collegium*, 1906, 141—142. Compare this vol., i, 446).—One gram of quebracho-tannin, either alone or with 100 grams of sodium acetate (compare Perkin and Yoshitake, *Trans.*, 1902, 81, 1164), is dissolved in 500 c.c. of water, and to the well-cooled solution 0.5 per cent. diazobenzene chloride solution is added, drop by drop, until a permanent turbidity appears. After twenty-four hours, the deposit formed is repeatedly extracted with boiling acetone. An amorphous product is thus obtained which melts above 360°, is insoluble in alcohol and other solvents, and gives, on analysis, the numbers: (1) C, 52.2; H, 3.18; and N, 14.55 per cent., when prepared without sodium acetate; and (2) C, 52.55, 54.40, and 59.90; H, 2.97, 3.18, and 4.00; N, 13.17, 14.50, and 14.55 per cent., when prepared by Perkin and Yoshitake's method. On boiling the azo-compound for forty hours with absolute alcohol and evaporating, there remains an amorphous, red, optically inactive residue, which dissolves in water or alcohol, gives all the reactions of a catechol-tannin, and contains 56.6 per cent. of carbon and 3.2 of hydrogen. This result tends to confirm the author's view (*Abstr.*, 1905, i, 914) that the activity of the colouring matter may depend on the sugar which accompanies it.

T. H. P.

**Derivatives of Dihydroisobenzofuran.** Parts I to III. ALFRED GUYOT and J. CATEL (*Bull. Soc. chim.*, 1906, [iii], 35, 551—562, 562—567, 567—571).—Most of the facts recorded in these papers have been published previously (*Abstr.*, 1905, i, 226, 516, 540). 2-Hydroxy-1:1:2-triphenyl-1:2-dihydroisobenzofuran (*Abstr.*, 1905, i, 226) separates from carbon disulphide in splendid crystals belonging to the monoclinic system, and is soluble in most organic solvents. *o*-Benzhydryltriphenylcarbinol (*loc. cit.*), produced by reducing the foregoing with sodium amalgam, when warmed in acetic acid solution with hydrochloric acid gives 1:1:2-triphenyl-1:2-dihydroisobenzofuran,  $C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ \text{CHPh} \end{smallmatrix} O$ , which crystallises from boiling alcohol in leaflets and melts at 120°. On oxidation with chromic acid, it is re-converted into the parent hydroxytriphenylisobenzofuran, and, like the latter, yields 9:10-diphenylanthracene when heated with sulphuric acid.

1:1-Diphenyl-1:2-dihydroisobenzofuran (*Abstr.*, 1905, i, 517) separates from organic solvents in colourless leaflets and melts at 93°.

T. A. H.

**Constitution of Hordenine.** EUGÈNE LÉGER (*Compt. rend.*, 1906, 143, 234—236. Compare this vol., i, 204).—The oxidation of hordenine by either alkaline or acid potassium permanganate or chromic acid yields only oxalic acid, whilst, when nitric acid is employed, picric acid is also obtained.

Hordenine methiodide, when treated with silver hydroxide, yield the methoxide, which, on distillation in an oil-bath, gives trimethyl amine; a dense, colourless oil, having an agreeable aromatic odour and volatile in a current of steam; and an amorphous, phenolic compound non-volatile at 180—190°.

On the basis of these results, the author suggests the formula  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$  for hordenine.

T. H. P.

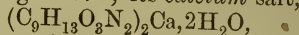
**Meroquinenine and the Constitution of the Cinchona Alkaloids.** WILHELM KOENIGS (*Annalen*, 1906, 347, 143—232).—The introduction to this paper contains a complete historical account of the investigations on the alkaloids of the cinchona bark. The researches which bear on the constitution of these alkaloids are discussed at length.

[With KARL BERNHART and JOSEF IBELE.]—Of the methods of preparing meroquinenine, namely, the hydrolysis of cinchenine with phosphoric acid, the hydrolysis of quinine, and the oxidation of cinchonine with chromic acid, the last mentioned is the most effective.

Pure meroquinenine melts and decomposes at 223—224° and has  $[\alpha]_D = 27.58$ —27.9° at 20° in a 10 per cent. aqueous solution (compare Abstr., 1894, i, 477). The *hydrochloride* forms colourless crystals melting at 146—148°, and the *aurichloride*, yellow needles which melt and decompose at 142°. The *monomethyl ether*,  $\text{C}_9\text{H}_{14}\text{O}_2\text{NMe}$ , prepared from the alkaloid and methyl alcohol in the presence of sulphuric acid, is a colourless oil which yields a crystalline *hydrochloride*; the *hydrochloride* of the *ethyl ether* crystallises in needles melting at 165°.

Meroquinenine yields an *acetyl* derivative,  $\text{C}_9\text{H}_{14}\text{O}_2\text{NAc}$ , which crystallises in plates melting at 110°; it still possesses faint basic properties, but at the same time has marked acid properties and yields a *silver salt*. The *ethyl ester* of the acetyl derivative is an oil.

*Nitrosomeroquinenine*,  $\text{C}_9\text{H}_{14}\text{O}_2\text{N} \cdot \text{NO}$ , prepared from the alkaloid and sodium nitrite in the presence of dilute sulphuric acid, forms colourless crystals melting at 67°; its *calcium salt*,

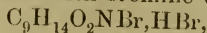


by means of which it is purified, is a soluble crystalline powder. The markedly acid properties of the acetyl and nitroso-derivatives show the presence of a carboxyl group, which is masked in the original alkaloid by the amino-group.

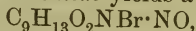
When meroquinenine is oxidised by a mixture of chromic and sulphuric acids, cincholeuponic acid is mainly formed, together with formic acid. When reduced with fuming hydriodic acid, meroquinenine is converted into cincholeupone,  $\text{C}_9\text{H}_{17}\text{O}_2\text{N}$ .

When meroquinenine is vigorously reduced with hydriodic acid and red phosphorus, 2-methyl-3-ethylpyridine is formed; the *picrate* crystallises in needles melting at 148—150°, and the *aurichloride* in yellow needles melting at 138°; when oxidised with permanganate, a mixture of 3:4-pyridinedicarboxylic and 4-methylpyridine-3-carboxylic acids is produced, the constitution of the pyridine being thus demonstrated.

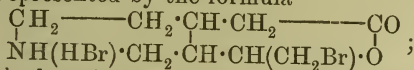
On treating meroquinenine with bromine water, a compound,



is formed, which can be reduced by zinc dust and sulphuric acid to meroquinenine. This *hydrobromide* yields a nitroso-derivative,



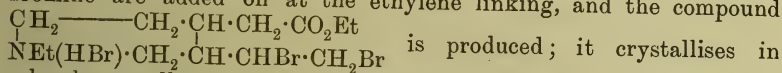
forming colourless crystals melting at  $98^\circ$  (compare Koenigs and Comstock, Abstr., 1884, 1382), which has, however, no acid properties, and is probably represented by the formula



in the action of the bromine water, the halogen is first of all added to the ethylene linking, and then one bromine atom eliminated with the hydrogen of the carboxyl group, a lactone ring being formed.

*Hydroxymeroquinenine*,  $\text{C}_9\text{H}_{14}\text{O}_2\text{N}\cdot\text{OH}$ , is obtained as a hydrochloride by boiling the hydrobromide just described with an aqueous suspension of silver chloride; it crystallises with  $\text{H}_2\text{O}$  and melts and decomposes at  $254^\circ$ ; the *hydrochloride* crystallises in needles melting and decomposing at  $208\text{--}210^\circ$ , and yields a *platinichloride* decomposing at  $240^\circ$ ; the *aurichloride* crystallises in needles, melting and decomposing at  $184^\circ$ . A *monoacetyl* derivative was obtained by heating the hydroxy-compound with acetic anhydride and isolated as an *aurichloride*,  $\text{C}_{11}\text{H}_{17}\text{O}_4\text{N}\cdot\text{HAuCl}_4$ , which melts and decomposes at  $214^\circ$ . Attempts to esterify hydroxymeroquinenine were unsuccessful.

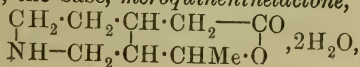
When the ethyl ester of meroquinenine is treated with ethyl iodide, the *ethyl* ester of *N-ethylmeroquinenine hydriodide*,  $\text{C}_9\text{H}_{13}\text{NEtO}_2\text{Et}\cdot\text{HI}$ , is obtained as colourless needles melting at  $156\text{--}157^\circ$ ; by treatment with silver chloride it can be converted into the corresponding *hydrochloride*, which crystallises in colourless prisms melting at  $220\text{--}221^\circ$ ; the corresponding *hydrobromide* melts at  $194^\circ$ . When boiled with aqueous hydrochloric acid, these esters are hydrolysed and the *hydrochloride* of *N-ethylmeroquinenine*,  $\text{C}_{11}\text{H}_{19}\text{O}_2\text{N}\cdot\text{HCl}$ , which melts at  $165^\circ$ , is produced. The base could not be obtained in a crystalline form. When the hydrobromide of the ethyl ester of *N-ethylmeroquinenine* is treated with bromine in chloroform solution, two atoms of bromine are added on at the ethylene linking, and the compound



is produced; it crystallises in colourless needles, melting and decomposing at  $182^\circ$ . When hydrolysed by boiling dilute hydrobromic acid, the *hydrobromide* of *N-ethyl-*

*bromomeroquinenine*,  $\begin{array}{c} \text{CH}_2\text{---CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{---CO} \\ | \qquad \qquad | \\ \text{NEt(HBr)}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}(\text{CH}_2\text{Br})\cdot\text{O} \end{array}$ , is formed, a lactone ring at the same time appearing; it crystallises in colourless needles melting and decomposing at  $218\text{--}220^\circ$ .

When meroquinenine is heated with a concentrated solution of arsenic acid at  $180\text{--}190^\circ$ , oxidation does not occur, but the elements of water are added, a hydroxydihydromeroquinenine being formed; when treated with hydrochloric acid, water is again eliminated, a *hydrochloride* melting and decomposing at  $255\text{--}256^\circ$  being produced, which is isomeric with the hydrochloride of meroquinenine. From this hydrochloride, the base, *meroquineninelactone*,





or *hydroxydihydromeroquinenine*, can be prepared, and crystallises in colourless prisms melting and decomposing at  $220^{\circ}$ . When the hydrochloride is treated with bromine or iodine and sodium hydroxide, bromoform and iodoform are respectively produced, reactions which indicate the presence of a methyl group as in the above formula.

On heating meroquinenine with hydrochloric acid, a meroquinenine lactone is not produced in any quantity, but the major portion of the base is converted into a levorotatory base, the *platinichloride* of which crystallises in yellow needles or leaflets melting and decomposing at  $232^{\circ}$ .

K. J. P. O.

**The Relations between Functional (Reactive) Groups in Remote Positions. Decamethyleneimine.** EDMOND E. BLAISE and L. HOUILLON (*Compt. rend.*, 1906, 143, 361—363. Compare this vol., i, 692).—By the action of heat on decamethylenediamine hydrochloride, a mixture of bases is obtained which contains a small quantity of 2-hexylpyrrolidine; the *platinichloride*, *aurichloride*, and *carbamide* of this base melt at  $117^{\circ}$ ,  $85^{\circ}$ , and  $146^{\circ}$  respectively, and are identical with the corresponding derivatives of 2-hexylpyrrolidine prepared synthetically by a similar method to that adopted in the synthesis of 2-butylpyrrolidine (*loc. cit.*).

*l*-Aminodecoic acid,  $\text{CO}_2\text{H}\cdot[\text{CH}_2]_8\cdot\text{CH}_2\cdot\text{NH}_2$ , prepared from brassylamic acid,  $\text{CO}_2\text{H}\cdot[\text{CH}_2]_9\cdot\text{CO}\cdot\text{NH}_2$ , can be crystallised from hot water and melts at  $187$ — $188^{\circ}$ ; the *hydrochloride* crystallises from hot water, and the *benzoyl* derivative crystallises from dilute alcohol in small nodules and melts at  $97^{\circ}$ . The properties of *l*-aminodecoic acid and its derivatives thus prepared are quite different from those ascribed by Krafft to the *l*-aminodecoic acid prepared from his so-called decamethyleneimine (Krafft and Phookan, *Abstr.*, 1892, 1180). It is probable, therefore, that decamethyleneimine does not exist, and that the reaction between functional groups in the same molecule is not a periodic function of the position of these groups.

M. A. W.

**Preparation of Pure Piperidine.** DANIEL VORLÄNDER and THEODOR WALLIS (*Annalen*, 1906, 345, 277—288. Compare this vol., i, 729, 730).—The velocity of oxidation of the purest commercial piperidine is so great, in comparison with that of diethylamine, as to render probable the occurrence of easily oxidisable impurities in the former. A purification can be effected by twice shaking an aqueous solution of piperidine (125 grams per litre) and sulphuric acid (250 grams per litre) with 70 grams of powdered potassium permanganate, the first time for ten minutes and the second time, with the recovered piperidine, for two to three hours. A better method is to treat nitrosopiperidine in acetone with solid permanganate for one to two days in the cold, or for three to four hours at a higher temperature. The piperidine recovered from the nitroso-compound in toluene by hydrogen chloride has a constant velocity of oxidation; the acetyl derivative boils at  $223^{\circ}$ , the hydrochloride melts at  $245^{\circ}$  (corr.), and the *platinichloride* at  $201.5^{\circ}$  (corr.).

From the precipitate obtained from the acetone solution during the oxidation, a dibasic *nitroso-acid* can be isolated, having the composition

$C_3H_6ON_2(CO_2H)_2$ , melting at  $79^\circ$ , and showing Liebermann's reaction. A neutral, colourless, crystalline substance,  $C_5H_{10}O_2NCl$  or  $C_5H_{12}O_2NCl$ , was also isolated; it melts at  $212^\circ$  and yields ethyl acrylate when heated. The presence of a partially hydrogenated pyridine in commercial piperidine was also indicated by the behaviour of acetyl piperidine towards bromine. The crude substance reacts with bromine to the extent of 17.5 per cent., whereas the acetyl compound obtained from purified piperidine does not react at all.

The oxidation velocity of other secondary amines, purified in a similar manner, is only slightly changed, except in the case of dipropylamine, the constant for which falls to about one-quarter of its original value.

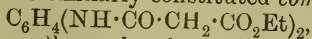
C. S.

**Transformation of Quinoline into 2-Methylindole.** MAURICE PADOA and A. CARUGHI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 113—118. Compare this vol., i, 530, 695).—When a mixture of quinoline vapour and hydrogen is passed through a tube containing reduced nickel at a temperature of  $260$ — $280^\circ$ , one part of the quinoline is converted into 2-methylindole and, after the opening of the closed nucleus, the remainder in part loses one carbon atom and in part two carbon atoms, giving rise to methyl-*o*-toluidine and *o*-toluidine. No methylindoline is formed in the reaction.

T. H. P.

**Ring-formation. II.** RICHARD MEYER (*Annalen*, 1906, 347, 17—54. Compare Abstr., 1903, i, 442).—The investigation of the action of dibasic acids on *o*-, *m*-, and *p*-diamines has been continued. [With G. VON LUTZAU.]—Malonanilide is readily obtained from aniline and excess of ethyl malonate.  $\alpha$ -Malon-naphthil,  $C_{10}H_7 \cdot N \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CH_2$ , is formed when  $\alpha$ -naphthylamine and ethyl malonate are heated for some hours. It crystallises in needles, melts above  $300^\circ$ , and is soluble in alkali hydroxides (compare Whiteley, *Trans.*, 1903, 83, 24).

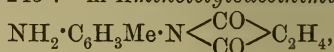
*o*-Phenylenemalonamide, prepared from *o*-phenylenediamine hydrochloride and the calculated quantity of sodium carbonate in presence of excess of ethyl malonate, crystallises in needles melting above  $300^\circ$ . The corresponding derivative of *o*-tolylenediamine crystallises in needles melting above  $300^\circ$ . No definite product could be obtained from *m*-phenylenediamine and ethyl malonate, but *m*-tolylenediamine [ $Me : (NH_2)_2 = 1 : 2 : 4$ ] and ethyl malonate yield ethyl *m*-tolylenedimalonamate,  $C_6H_3Me(NH \cdot CO \cdot CH_2 \cdot CO_2Et)_2$ , which is a white, amorphous powder melting at  $110$ — $113^\circ$ . *p*-Phenylenediamine and ethyl malonate yield the similarly constituted compound,



which crystallises in needles and melts at  $164^\circ$ .

Aniline and ethyl succinate yield succinil, similarly  $\alpha$ -naphthylamine yields  $\alpha$ -succinonaphthil, but  $\beta$ -naphthylamine gives the ester of ethyl  $\beta$ -naphthylsuccinamate,  $C_{10}H_7NH \cdot CO \cdot C_2H_4 \cdot CO_2Et$ , which crystallises in needles and melts at  $99$ — $100^\circ$ . The condensation products prepared from *o*-phenylenediamine or *o*-tolylenediamine and ethyl succinate could not be purified satisfactorily. From *m*-phenylenediamine and ethyl succinate, a compound is obtained, crystallising in

needles and melting at  $205^{\circ}$ , the chemical nature of which could not be established; with ammonia it yields *m*-phenylenedisuccinamide,  $C_6H_4(NH \cdot CO \cdot C_2H_4 \cdot CO \cdot NH_2)_2$ , which crystallises in needles melting and decomposing at  $245^{\circ}$ . *m*-Aminotolylsuccinimide,



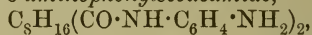
is formed from *m*-tolylenediamine and crystallises in needles melting at  $256$ — $259^{\circ}$ . *p*-Phenylenediamine yields *p*-aminosuccinil (*loc. cit.*).

[With P. JAEGER.]—With ethyl isosuccinate, the diamines yield similar compounds. *o*-Phenylenesisosuccinimide,  $C_6H_4 \begin{array}{c} \diagup NH \cdot CO \\ \diagdown NH \cdot CO \end{array} CHMe$ , crystallises in yellow plates, melting above  $350^{\circ}$ ; at the same time, a base,  $CHMe(CO \cdot NH \cdot C_6H_4 \cdot NH_2)_2$ , which is purified in the form of a *picrate*, is produced; the latter crystallises in yellow plates and melts and decomposes at  $245$ — $250^{\circ}$ ; the base, which could not be purified, crystallises in slender needles.

*m*-Phenylenediamine and ethyl isosuccinate yield an insoluble compound melting at  $275$ — $280^{\circ}$ . From *p*-phenylenediamine, ethyl *p*-phenylenediisusuccinamate,  $C_6H_4(NH \cdot CO \cdot CHMe \cdot CO_2Et)_2$ , is formed. It crystallises in needles and melts at  $180$ — $181^{\circ}$ . The condensation product from *m*-tolylenediamine could not be isolated in the pure state. *o*-Tolylenediamine yields similarly a mixture of *o*-tolyleneisusuccinamide and the basic *di*-*o*-aminotolylisusuccinamide, which are separated by treatment with dilute acetic acid; the former crystallises in needles or plates, the latter in needles, and yields a *picrate* which crystallises in yellow needles melting and decomposing at  $235$ — $240^{\circ}$ .

Ethyl adipate reacts with *o*-phenylenediamine, yielding in small amount a basic, crystalline substance which could not be purified.

[With JOH. MAIER.]—Ethyl sebacate yields with *o*-phenylenediamine two compounds: *o*-phenylenesebacamide,  $C_6H_4 \begin{array}{c} \diagup NH \cdot CO \\ \diagdown NH \cdot CO \end{array} C_8H_{16}$ , crystallises in needles melting at  $134$ — $135^{\circ}$ , and is indifferent towards both acids and bases. *Di*-*o*-aminophenylsebacamide,



crystallises in needles melting above  $320^{\circ}$ . Ethyl *m*-phenylenedisebacate,  $C_6H_4(NH \cdot CO \cdot C_8H_{16} \cdot CO_2Et)_2$ , is prepared by the condensation of *m*-phenylenediamine with the ester, and crystallises in microscopic needles melting at  $97^{\circ}$ ; at the same time a yellow, insoluble powder is formed. *p*-Phenylenediamine and ethyl sebacate yield several products, of which *p*-aminosebacanil,  $NH_2 \cdot C_6H_4 \cdot N \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} C_8H_{16}$ , can be isolated; it crystallises in needles melting at  $150$ — $151^{\circ}$ .

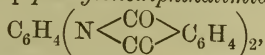
[With P. JAEGER.]—The condensations of the chlorides of dibasic acids with aromatic diamines have been investigated. With succinyl chloride, *o*-phenylenediamine yields *di*-*o*-aminophenylsuccinamide, whilst *m*-phenylenediamine and *p*-phenylenediamine do not give condensation products, but merely succinates of the base. With *o*-tolylenediamine, *di*-*o*-aminotolylsuccinamide,  $C_2H_4(CO \cdot NH \cdot C_6H_3Me \cdot NH_2)_2$ , is formed, and crystallises in needles melting above  $320^{\circ}$ ; the *hydrochloride* was analysed.

Adipic chloride and *o*-phenylenediamine yield *di*-*o*-aminophenyl-



*adipamide*, which was isolated as *hydrochloride*; the latter crystallised in long needles.

From phthalyl chloride and *o*-phenylenediamine, *di-o-aminophenyl-phthalamide*,  $C_6H_4(CO \cdot NH \cdot C_6H_4 \cdot NH_2)_2$ , was prepared as colourless needles. At the same time, *o*-phenylenephthalamide was formed, and also *o*-phenylenediphthalimide, the latter being generally the main product of the reaction. Phthalyl chloride and *o*-tolylenediamine gave *o*-tolylenediphthalimide. Phthalyl chloride and *p*-phenylenediamine yield *p*-aminophthalanil and *p*-phenylenediphthalimide,



which crystallises in needles or in rhombic plates and melts at  $356^\circ$ .

K. J. P. O.

**Constitution of Nitroimines and Action of Phenylcarbimide on Methylnitroamine.** ROLAND SCHOLL (*Annalen*, 1906, 345, 363—384. Compare Abstr., 1905, i, 181; Angelucci, *ibid.*, i, 801; Angeli and Castellana, this vol., i, 162).—In addition to the evidence adduced previously (*loc. cit.*), the following arguments are advanced in

favour of the nitroimine formula,  $>CH \cdot \overset{|}{C} \cdot N \cdot NO_2$ . (1) The behaviour of the nitroimines towards alkalis resembles that of secondary nitroamines. (2) The fact that the nitroimines are pseudo-acids and yield *N*- and *O*-alkyl derivatives cannot be brought into line with Angeli and Castellana's "pernitroso" formula. (3) Reducing agents generally eliminate an atom of nitrogen; in some cases, however, hydrazine derivatives are obtained. (4) Nitroimines, as a class, give the Thiele-Lachmann nitroamine reaction; the nitroimines obtained from the oximes of pinacolin, santonin, menthone, and mesityl oxide give, like most nitroamines, the Liebermann reaction. Camphornitroimine gives colour reactions with phenol and sulphuric acid, but the author does not assert positively that these are due to Liebermann's reaction. (5) The occurrence of camphanazine, nitrogen, camphene, and camphor-oxime among the reduction products of camphornitroimine can be explained rationally by the nitroimine formula, and does not require the assumption of the existence of the otherwise quite unknown "pernitroso" group.

[With KARL HOLDERMANN.]—*α-Nitro-β-phenyl-α-methylcarbamide*,  $NHPh \cdot CO \cdot N(NO_2)Me$ , is obtained by the reaction of methylnitroamine and "active" phenylcarbimide (phenylcarbimide containing phenylcarbamate), dry ether being added when the temperature rises to  $35-40^\circ$ . With ordinary phenylcarbimide the reaction proceeds slowly, but more rapidly after the addition of a small quantity of carbamide. The colourless crystals, after the removal of *s*-diphenylcarbamide by acetone and light petroleum, sinter at  $68^\circ$  and melt and decompose at  $74.5-75^\circ$ . It gives Liebermann's reaction, is decomposed by boiling water, and with ammonia (or aniline) in ether at the ordinary temperature yields phenylcarbamide (or diphenylcarbamide) and methyl-nitroamine.

*s-Nitrophenylmethylcarbamide*,  $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NHMe$ , results from the action of ethyl nitrate on *s*-phenylmethylcarbamide in concentrated sulphuric acid at  $-5^\circ$ . The yellow product is boiled with one

per cent. sodium hydroxide, cooled, and the residue crystallised from hot acetic acid. The substance forms colourless prisms, becomes yellow at 190—200°, and melts at 230—231°. Hot dilute sodium hydroxide solution dissolves it to a yellow solution, from which the substance is recovered unchanged on cooling. The presence of the nitro-group in the benzene nucleus is deduced from the fact that the substance gives neither the Liebermann nor the Thiele-Lachmann nitroamine reaction.

*s*-Dinitrophenylmethylcarbamide,  $C_6H_3(NO_2)_2 \cdot NH \cdot CO \cdot NHMe$ , results when twice the quantity of ethyl nitrate is used in the preceding preparation; it forms yellow needles, melts and decomposes at 206—207°, and resembles the preceding compound in its behaviour. C. S.

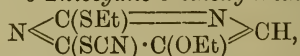
**Constitution of Scholl's Nitroimines.** OTTORINO ANGELUCCI (*Gazzetta*, 1906, 36, i, 627—628. Compare Abstr., 1905, i, 801).—The author criticises the work of Scholl (preceding abstract), who states that the nitroimines react with secondary amines according to the equation  $:C:N \cdot NO_2 + NH_2R = :C:NR + H_2NO_2 \rightarrow H_2O + N_2O$ . In the cold, however, camphornitroimine reacts with methylamine, giving water and nitrous oxide, which products cannot be regarded as derived from the decomposition of the nitroamide, since this is stable under the conditions of the experiment.

Further, Scholl states that all nitroimines give the reaction of Liebermann and that of Thiele and Lachmann. The author finds that pernitrosocamphor gives no trace of Liebermann's reaction.

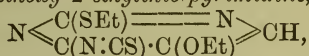
T. H. P.

**Benzenesulphomethylguanidine.** D. ACKERMANN (*Zeit. physiol. Chem.*, 1906, 48, 382. Compare this vol, ii, 505).—Methylguanidine reacts with benzenesulphonic chloride yielding *benzenesulphomethylguanidine*, which melts at 184°; its solubility in water at the ordinary temperature is 0.04 in 100. J. J. S.

**Pyrimidines: Action of Potassium Thiocyanate on Imide Chlorides.** XV. TREAT B. JOHNSON and ELMER V. MCCOLLUM (*Amer. Chem. J.*, 1906, 36, 136—148. Compare this vol., i, 704; Wheeler and Merriam, Abstr., 1901, i, 514; Wheeler and Bristol, Abstr., 1905, i, 483).—6-Thiocyano-5-ethoxy-2-ethylthiopyrimidine,



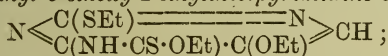
prepared by boiling 6-chloro-5-ethoxy-2-ethylthiopyrimidine with potassium thiocyanate in 95 per cent. alcoholic solution, crystallises from alcohol in lemon-yellow prisms, melts at 66—67°, and dissolves in concentrated hydrochloric acid, being reprecipitated by alkali hydroxides or on dilution. It reacts with thiobenzoic or thioacetic acid with development of heat, forming 6-thio-5-ethoxy-2-ethylthiopyrimidine,  $NH \begin{array}{c} \diagup C(SET) \\ \diagdown CS \cdot C(OEt) \end{array} \begin{array}{c} = \\ = \\ = \end{array} N \begin{array}{c} \diagup \\ \diagdown \end{array} CH$ , which is prepared also by boiling 6-chloro-5-ethoxy-2-ethylthiopyrimidine with alcoholic potassium sulphide; it crystallises from alcohol in yellow prisms and melts at 144—145°.

*6-Thiocarbimido-5-ethoxy-2-ethylthiolpyrimidine,*

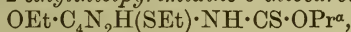
is formed when the 6-thiocyanopyrimidine is heated at 105—110°; it solidifies over concentrated sulphuric acid, melts at 45—50°, boils at 228—235° under 20—23 mm. pressure, is exceedingly hygroscopic, and when treated with ammonia yields *6-thiocarbamido-5-ethoxy-*

*2-ethylthiolpyrimidine,*  $\text{N} \begin{array}{c} \text{C(SET)} \\ \text{C(NH \cdot CS \cdot NH_2) \cdot C(OEt)} \end{array} \text{N} \text{CH},$  which crystallises from alcohol in yellow prisms and melts at 172°.

When 6-chloro-5-ethoxy-2-ethylthiolpyrimidine is boiled with potassium thiocyanate in alcoholic solution, the cyanothiol formed changes slowly into the thiocarbimido-derivative, which reacts with alcohol, forming *ethyl 5-ethoxy-2-ethylthiolpyrimidine-6-thiocarbamate,*

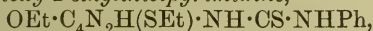


this crystallises in long prisms, melts at 93—94°, volatilises to some extent when evaporated with alcohol, and is soluble in aqueous sodium hydroxide.

*n-Propyl 5-ethoxy-2-ethylthiolpyrimidine-6-thiocarbamate,*

formed similarly by boiling 6-chloro-5-ethoxy-2-ethylthiolpyrimidine with potassium thiocyanate in *n*-propyl-alcoholic solution, crystallises in small prisms and melts at 56—57°.

The following thiocarbamido-derivatives are prepared by heating 6-thiocyano-5-ethoxy-2-ethylthiolpyrimidine at 150—160° and treating the product with the aromatic base in benzene solution. *6-Phenylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine,*

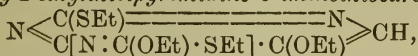


forms distorted prisms and melts at 82—83°. *6-p-Tolylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine,*  $\text{C}_{16}\text{H}_{20}\text{ON}_4\text{S}_2$ , forms stellate clusters of needles and melts at 115°. *6-o-Tolylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine,*  $\text{C}_{16}\text{H}_{20}\text{ON}_4\text{S}_2$ , crystallises in rhombic prisms and melts at 129—130°. *6-p-Anisylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine,*  $\text{OEt} \cdot \text{C}_4\text{N}_2\text{H(SET)} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , crystallises from alcohol in rhombic prisms and melts at 122—123°. *6-m-Nitrophenylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine,*  $\text{C}_{15}\text{H}_{17}\text{O}_3\text{N}_5\text{S}_2$ , forms slender prisms and melts at 161°.

G. Y.

**Pyrimidines: Formation of Purines from Carbamido-pyrimidines.** XVI. TREAT B. JOHNSON and ELMER V. MCCOLLUM (*Amer. Chem. J.*, 1906, 36, 149—159. Compare preceding abstract and this vol., i, 704).—*Ethyl formylglycollate*,  $\text{OEt} \cdot \text{CH}(\text{COH}) \cdot \text{CO}_2\text{Et}$ , is obtained on addition of hydrochloric acid to its sodium salt as a colourless oil which boils at 115—118° under 35 mm. pressure.

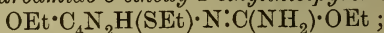
2:6-Dioxy-5-ethoxypyrimidine is readily prepared by boiling 5-ethoxy-2-methylthiolpyrimidine with hydrochloric acid.

*Ethyl 5-ethoxy-2-ethylthiolpyrimidine-6-iminothiocarbonate,*

is prepared by [the action of ethyl bromide and sodium on ethyl

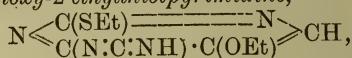


5-ethoxy-2-ethylthiopyrimidine-6-thiocarbamate in alcoholic solution; it is obtained as an oil which reacts with ammonia in alcoholic solution, forming 6- $\psi$ -ethylcarbamido-5-ethoxy-2-ethylthiopyrimidine,



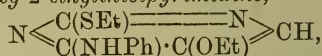
this crystallises from light petroleum, melts at  $77^\circ$ , and is converted slowly by concentrated hydrochloric acid into 6-carbamido-5-ethoxy-2-ethylthiopyrimidine,  $\text{OEt} \cdot \text{C}_4\text{N}_2\text{H}(\text{SEt}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , which forms prismatic crystals and melts and decomposes at  $166\text{--}167^\circ$ .

6-Cyanamino-5-ethoxy-2-ethylthiopyrimidine,

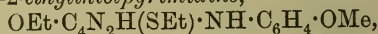


prepared by boiling 6- $\psi$ -ethylcarbamido-5-ethoxy-2-ethylthiopyrimidine with sodium in benzene solution for forty hours, crystallises in white prisms, melts and effervesces slightly at  $167\text{--}168^\circ$ , is soluble in aqueous alkali hydroxides, is reprecipitated by acids, and is decomposed slowly by boiling water. The hydrochloride forms slender prisms and melts and decomposes at  $175\text{--}180^\circ$ .

6-Anilino-5-ethoxy-2-ethylthiopyrimidine,



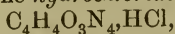
formed by boiling 6-chloro-5-ethoxy-2-ethylthiopyrimidine with aniline in alcoholic solution, crystallises from light petroleum in large prisms and melts at  $60^\circ$ . 6-p-Toluidino-5-ethoxy-2-ethylthiopyrimidine crystallises in long prisms, melts at  $72^\circ$ , and yields a hydrochloride,  $\text{C}_{15}\text{H}_{19}\text{ON}_3\text{S} \cdot \text{HCl}$ , which forms hair-like crystals and melts and decomposes at  $105\text{--}106^\circ$ . 6-o-Toluidino-5-ethoxy-2-ethylthiopyrimidine,  $\text{C}_{15}\text{H}_{19}\text{ON}_3\text{S}$ , crystallises from alcohol in flat prisms and melts at  $80^\circ$ ; the hydrochloride,  $\text{C}_{15}\text{H}_{19}\text{ON}_3\text{S} \cdot \text{HCl}$ , forms prisms and decomposes at  $140\text{--}145^\circ$ , or when dissolved in water. 6-p-Anisidino-5-ethoxy-2-ethylthiopyrimidine,



crystallises from alcohol in stout prisms and melts at  $68\text{--}69^\circ$ ; the hydrochloride,  $\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}_3\text{S} \cdot \text{HCl}$ , forms prismatic crystals. 6-m-Nitroanilino-5-ethoxy-2-ethylthiopyrimidine,  $\text{C}_{14}\text{H}_{16}\text{O}_3\text{N}_4\text{S}$ , crystallise in long needles and melts at  $125^\circ$ ; the hydrochloride melts and decomposes at  $125\text{--}135^\circ$ .

G. Y.

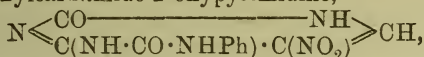
Pyrimidines: 5 Nitrocytosine and its Reduction to 5:6 Diamino-2-oxypyrimidine. XVII. TREAT B. JOHNSON, CARL C. JOHNS, and FREDERICK W. HEYL (*Amer. Chem. J.*, 1906, 36, 160—177).—Nitrocytosine (Wheeler and Johnson, *Abstr.*, 1904, 624), which is formed in an 83.5 per cent. yield by the action of nitric acid of sp. gr. 1.5 on 6-amino-2-ethylthiopyrimidine, is 5-nitro-6-amino-2-oxypyrimidine,  $\text{N} \begin{array}{c} \text{CO} \\ \text{C}(\text{NH}_2) \end{array} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \text{NH} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \text{CH}$ , as (1) it yields nitrouracil when heated with 20 per cent. sulphuric acid in a sealed tube at  $185\text{--}197^\circ$ , or when heated with nitrosyl chloride in aqueous hydrochloric acid solution in a sealed tube at  $85\text{--}95^\circ$ , and (2) it does not react with bromine. The hydrochloride of 5-nitrocytosine,



forms clusters of prisms and does not decompose below  $300^\circ$ .

The action of nitric acid of sp. gr. 1.5 on 5-bromo-6-amino-2-ethylthiopyrimidine leads to the formation of 5-bromocytosine.

5-Nitro-6-phenylcarbamido-2-oxypyrimidine,

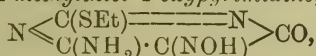


formed by heating 5-nitrocytosine with phenylthiocarbimide at 100°, decomposes, but does not melt, above 215°, and is insoluble in all solvents.

When boiled with acetic anhydride, 5-nitrocytosine yields mixtures of the *mono*- and *di*-acetyl derivatives; the latter,  $\text{C}_8\text{H}_8\text{O}_5\text{N}_4$ , forms needle-like prisms and decomposes at 273—275°.

5 : 6-Diamino-2-oxypyrimidine,  $\text{N} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{NH}_2) \end{array} \text{NH} \rangle \text{CH}, \text{H}_2\text{O}$ , is prepared by reduction of 5-nitrocytosine with aluminium amalgam and water below 35°; it forms clusters of prisms, loses  $\text{H}_2\text{O}$  at 120—130°, decomposes above 230°, forms an insoluble, red precipitate with potassium bismuth iodide, reduces platinum, gold, silver, and Fehling's solutions, has an alkaline reaction to litmus, and is precipitated by phosphotungstic acid. The *picrate*,  $\text{C}_4\text{H}_6\text{ON}_4, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , forms spherical aggregates of prisms, commences to become brown at about 170°, and decomposes when more highly heated; the *mercurichloride*,  $\text{C}_4\text{H}_6\text{ON}_4, \text{HgCl}_2$ , was analysed.

6-Amino-5-nitroso-2-methylthiol-4-oxypyrimidine,

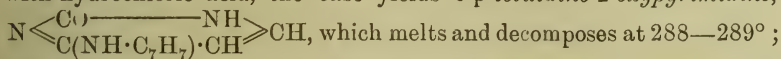


prepared by the action of sodium nitrite and glacial acetic acid on 6-amino-2-methylthiol-4-oxypyrimidine in aqueous sodium hydroxide solution, is reduced by ammonium sulphide to 5 : 6-diamino-2-methyl-

thiol-4-oxypyrimidine,  $\text{N} \begin{array}{c} \text{C}(\text{SEt}) \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{NH}_2) \end{array} \text{NH} \rangle \text{CO}$ , which crystallises in needles or prisms, melts and decomposes at 215—216°, is readily soluble in alcohol, and becomes red when exposed to air.

6-*p*-Toluidino-2-ethylthiopyrimidine,  $\text{N} \begin{array}{c} \text{C}(\text{SEt}) \\ \diagup \quad \diagdown \\ \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \cdot \text{CH} \end{array} \text{N} \rangle \text{CH}$ ,

prepared by heating 6-chloro-2-ethylthiopyrimidine with *p*-toluidine in benzene solution, crystallises in prisms, melts at 104°, and is readily soluble in alcohol or benzene; the *hydrochloride*,  $\text{C}_{13}\text{H}_{15}\text{N}_3\text{S}, \text{HCl}$ , crystallises in needles and decomposes at 198—207°. When boiled with hydrochloric acid, the base yields 6-*p*-toluidino-2-oxypyrimidine,



which melts and decomposes at 288—289°; the *hydrochloride*,  $\text{C}_{11}\text{H}_{11}\text{ON}_3, \text{HCl}$ , forms microscopic prisms and decomposes at 180—190°.

6-*o*-Toluidino-2-ethylthiopyrimidine,  $\text{N} \begin{array}{c} \text{C}(\text{SEt}) \\ \diagup \quad \diagdown \\ \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \cdot \text{CH} \end{array} \text{N} \rangle \text{CH}$ ,

prepared from 6-chloro-2-ethylthiopyrimidine and *o*-toluidine, crystallises from alcohol in prisms and melts at 87°; the *hydrochloride*  $\text{C}_{13}\text{H}_{15}\text{N}_3\text{S}, \text{HCl}$ , forms granular crystals and melts and decomposes at 230—232°. When boiled with hydrochloric acid, the base forms

6-*o*-toluidino-2-oxypyrimidine,  $\text{N} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \cdot \text{CH} \end{array} \text{NH} \rangle \text{CH}$ , which

crystallises in stellate clusters of prisms and decomposes at  $262^{\circ}$ ; the *hydrochloride*,  $C_{11}H_{11}(ON_3)HCl$ , forms lenticular crystals and decomposes at  $227-231^{\circ}$ .

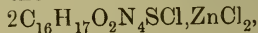
6-*p*-Anisidino-2-ethylthiopyrimidine,  $SEt \cdot C_4N_2H_2 \cdot NH \cdot C_6H_4 \cdot OMe$ , is obtained as an oil; the *hydrochloride*,  $C_{13}H_{15}(ON_3)S \cdot HCl$ , crystallises in needles and melts and decomposes at  $200-201^{\circ}$ . 6-*p*-Anisidino-2-oxypyrimidine,  $C_{11}H_{11}O_2N_3$ , melts at  $262^{\circ}$ ; the *hydrochloride*,  $C_{11}H_{11}O_2N_3 \cdot HCl$ ,

decomposes at  $145-165^{\circ}$ .

6-*m*-Nitro-2-ethylthiopyrimidine,  $SEt \cdot C_4N_2H_2 \cdot NH \cdot C_6H_4 \cdot NO_2$ , melts at  $175^{\circ}$ ; the *hydrochloride*,  $C_{12}H_{12}O_2N_4S \cdot HCl$ , forms needles and decomposes at  $140-155^{\circ}$ . 6-*m*-Nitro-2-oxypyrimidine,  $C_{10}H_8O_3N_4$ , is formed by boiling the preceding compound with hydrobromic acid; it crystallises in needle-like prisms and decomposes above  $275^{\circ}$ .

G. Y.

**Methylene-green.** EUGÈNE GRANDMOUGIN and E. WALDER (*Zeit. Farb. Ind.*, 1906, 5, 285-286).—The view that methylene-green is nitromethylene-blue (Gnehm and Walder, this vol., i, 390) is confirmed by the fact that it can be prepared by nitrating methylene-blue dissolved in 40 per cent. acetic acid with 50 per cent. nitric acid. The dye is separated in the form of the *zincochloride*,



which forms a dark brownish-violet, non-crystalline powder. The *hydriodide*,  $C_{16}H_{16}O_2N_4S \cdot HI \cdot H_2O$ , forms long, violet needles and crystallises well from water.

W. A. D.

**Aromatic Azocyanamides.** PAUL PIERRON (*Compt. rend.*, 1906, 143, 340-344).—*Benzeneazo-p-cyananilide*,  $Ph \cdot N_2 \cdot C_6H_4 \cdot NH \cdot CN$ , prepared by the action of diazobenzene chloride on the sodium derivative of cyananilide according to the equation  $Ph \cdot N_2 \cdot Cl + NHPh \cdot CN = Ph \cdot N_2 \cdot C_6H_4 \cdot NH \cdot CN + NaCl$ , or by the action of an alcoholic solution of cyanogen chloride or bromide on *p*-aminoazobenzene in the presence of alkali hydrogen carbonates, forms yellow, flattened needles, melts at  $163^{\circ}$ , is readily soluble in alcohol, slightly so in benzene or ether, and almost insoluble in water; its alkaline solutions dye wool silk, or mordanted cotton light yellow; it is hydrolysed by dilute acids, yielding the corresponding carbamide, *benzeneazo-p-phenylcarbamide*,  $Ph \cdot N_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$ , which crystallises from alcohol in brownish-yellow needles, melts at  $231^{\circ}$ , is insoluble in water, slightly soluble in ether, chloroform, or benzene, more so in alcohol. The *benzoyl* derivative,  $Ph \cdot N_2 \cdot C_6H_4 \cdot NBz \cdot CN$ , forms short, hard, orange prisms, melts at  $161^{\circ}$ , is soluble in alcohol, and slightly so in benzene. *Benzeneazo-p-cyananilide* is reduced by stannous chloride, yielding aniline and *p*-aminophenylcarbamide, and reacts with hydroxylamine to form *p*-aminoazobenzene and phenylcarbamide.

*Benzeneazo-p-cyano-o-toluidide*,  $Ph \cdot N_2 \cdot C_6H_3Me \cdot NH \cdot CN$ , prepared similarly to the above compound, which it closely resembles, melts at  $159^{\circ}$ ; the *carbamide* and *benzoyl* derivatives melt at  $207^{\circ}$  and  $141^{\circ}$  respectively.



*Benzeneazo-p-cyano-m-toluidide*,  $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{CN}$ , forms light yellow, pliable, silky needles, and melts at  $118-119^\circ$  when gently or at  $105^\circ$  when rapidly heated; the *carbamide* and *benzoyl* derivatives melt at  $152^\circ$  and  $134^\circ$  respectively, and form long, flexible needles, the former dull reddish-yellow, the latter brilliant orange. *Benzeneazo- $\alpha$ -cyanonaphthylamide*,  $\text{Ph}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{CN}$ , forms a violet-red powder with a green reflex, melts indefinitely at  $176-180^\circ$ , and is very hygroscopic; the *carbamide* derivative melts at  $253^\circ$ .

*Benzeneazo-o-ethoxy-p-cyanoanilide*,  $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{NH}\cdot\text{CN}$ , melts at  $121^\circ$  and crystallises from a mixture of light petroleum and benzene in orange-yellow needles; the *carbamide* derivative forms light yellow needles and melts at  $206^\circ$ .

*p*-Cyanotoluidide forms an unstable compound, probably the diazo-cyanamide,  $\text{Ph}\cdot\text{N}_2\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Me}$ , with diazobenzene chloride, which rapidly decomposes, yielding a tarry, black mass containing the original cyanamide, the corresponding carbamide, and *p*-hydroxyazobenzene. The following equations indicate the probable course of the reactions:

$$\text{Ph}\cdot\text{N}_2\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Me} + \text{H}_2\text{O} = \text{PhOH} + \text{N}_2 + \text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CN};$$

$$\text{Ph}\cdot\text{N}_2\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Me} + \text{PhOH} = \text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH} + \text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CN}.$$

M. A. W.

**Salts of Benzeneazophenyltrimethylammonium.** DANIEL VORLÄNDER, A. LOGOTHETIS, and A. J. PEROLD (*Annalen*, 1906, 345, 303—314).—The iodide, prepared from methyl iodide and dimethyl-aminoazobenzene, separates from water at  $80^\circ$  in orange-yellow crystals which melt at  $184^\circ$ , and from methyl or amyl alcohol in brown or orange-red crystals which melt at  $173^\circ$ .

The iodide, precipitated by potassium iodide from a solution of benzeneazophenyltrimethylammonium chloride, melts at  $178^\circ$ , and after crystallisation from alcohol at  $175^\circ$ . By crystallisation from water, the melting point of the former substance rises to  $183^\circ$ , whereas that of the latter, after repeated crystallisation from alcohol, falls to  $170-173^\circ$ .

The *bromide*, prepared by shaking the iodide and silver bromide in water or alcohol, separates from water at  $80^\circ$  in crystals which melt at  $196^\circ$ , and from alcohol in leaflets melting at  $192^\circ$ . The leaflets occur in three forms. All these crystals, according to crystallographic measurements, belong to the same, probably to the rhombic, system.

The *chloride*, obtained from the iodide and silver chloride, separates from water in orange prisms, melts at  $194^\circ$ , and contains 1—2 mols.  $\text{H}_2\text{O}$ . The *zinc* salt,  $(\text{C}_{15}\text{H}_{18}\text{N}_3\text{Cl})_2\cdot\text{ZnCl}_2$ , separates from water in orange-yellow plates, melts at  $201^\circ$ , and contains  $2\text{H}_2\text{O}$ . The *platinichloride*,  $(\text{C}_{15}\text{H}_{18}\text{N}_3)_2\cdot\text{PtCl}_6$ , forms orange-yellow needles and melts and decomposes at  $195-198^\circ$ . The *nitrate* melts at  $216^\circ$ . The *picrate* forms yellow needles. The *carbonate* is obtained by evaporating in a vacuum a solution of the hydroxide saturated with carbon dioxide; it forms orange-red plates. The aqueous solution of the free base has a deep orange colour and an alkaline reaction; when freshly prepared it is odourless, but after some time acquires the odour of trimethylamine. By boiling

or by evaporation in a vacuum at 30—35° the solution decomposes and yields methylated amines, ammonia, dimethylaniline, *p*-dimethylaminoazobenzene, and a substance which melts at 126—127° and is sparingly soluble in hot water.

Aniline and not methylaniline results by the reduction of benzeneazophenyltrimethylammonium chloride by stannous chloride and hydrochloric acid; the chloride is therefore an ammonium-azo-compound,  $\text{NPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{X}$ , and not a quinone phenylhydrazone,  $\text{NPhMe:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{X}$ . C. S.

**Isomerism among the Hydroxyazo-compounds: 5-Azoisoeugenols.** ERNESTO PUXEDDU (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 128—136).—The azo-derivatives of isoeugenol, like those of eugenol (Oddo and Puxeddu, *Abstr.*, 1905, i, 492), have the azo-group in the 5-position, taking the position of the propenyl group as 1. The change in the nature of the  $\text{C}_3\text{H}_5$  substituent from allyl in the eugenol compounds to propenyl in the isoeugenol derivatives is accompanied by considerable changes in the physical and chemical characters. Thus, the azoisoeugenols cannot be obtained in a crystalline condition from alcohol or other solvents. They dissolve in dilute alkali hydroxide solutions, but do not separate out, as do the azoeugenols, without the addition of carbon dioxide or a mineral acid. When heated, they decompose without showing any definite melting point. They are not reduced by phenylhydrazine. On boiling with acetic anhydride and fused sodium acetate, they yield amorphous acetyl derivatives, which, when separated by the addition of water, emit an agreeable aromatic odour resembling that of raspberries.

Benzeneazoisoeugenol (compare Borsche and Streitberger, *Abstr.*, 1904, i, 1064) is obtained as a brick-red, amorphous powder, which dissolves in concentrated sulphuric acid, giving an intense brown coloration, and ignites on contact with fuming nitric acid. Its ethereal solution, on adding ethereal ferric chloride solution, assumes a brown colour.

*o*-Tolueneazoisoeugenol,  $\text{C}_6\text{H}_4\text{Me:N}_2\cdot\overset{\text{OH}\cdot\text{C}\cdot\text{C}(\text{OMe})\cdot\text{CH}}{\underset{\text{CH}}{\underset{\text{CH}}{\text{C}}}}\cdot\text{CH}=\text{C}\cdot\text{CH}\cdot\text{CHMe}$ , is a reddish-brown powder, readily soluble in the ordinary organic solvents, excepting light petroleum and carbon tetrachloride, in which it dissolves only sparingly. It begins to darken and decompose at 62°.

*m*-Tolueneazoisoeugenol,  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_2$ , forms a red powder which begins to decompose at about 100°, and dissolves slightly in light petroleum or carbon tetrachloride and readily in other organic solvents. Concentrated sulphuric acid dissolves it, giving an intensely brown solution, and nitric acid causes it to ignite.

$\beta$ -Naphthaleneazoisoeugenol,  $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_2$ , is obtained as a brick-red powder, which dissolves readily in the more common organic solvents.  $\alpha$ -Naphthaleneazoisoeugenol is an amorphous, reddish-brown powder, which decomposes without melting.

*o*-Nitrobenzeneazoisoeugenol is a reddish-brown powder which begins to decompose at about 120°, and dissolves readily in organic solvents. *p*-Nitrobenzeneazoisoeugenol was also prepared. T. H. P.

**Chemical Action of Light.** ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 136—138).—On subjecting *s*-tribromodiazobenzene *syn*-cyanide, in benzene solution, to the action of light for three days, it is completely transformed into the corresponding *anti*-compound (compare Hantzsch and Schultze, *Abstr.*, 1895, i, 348).

T. H. P.

**Action of Dilute Hydrochloric Acid on Albumins.** ED. SWIRLOWSKY (*Zeit. physiol. Chem.*, 1906, 48, 252—299. Compare Lawroff, *Abstr.*, 1905, ii, 178).—The prolonged action of 0.5 per cent. hydrochloric acid on the following proteids at 36—38° has been investigated, care being taken that putrefaction did not occur and that proteolytic enzymes were absent: gelatin, albumin from the blood serum of horses, casein, crystallised hæmoglobin from horse's blood, and albumoses obtained from Witt's peptone. The effects produced by the acid are similar to those observed during peptic digestion, but the reaction proceeds far more slowly. Monoamino-acids or combinations of such acids are formed; these are not precipitated by phosphotungstic acid and are decomposed by 20 per cent. hydrochloric or sulphuric acid into free amino-acids. The intensity of the action is different with the different proteids. Gelatin is least readily hydrolysed, so that at the end of 150 days the presence of free amino-acids cannot be demonstrated, as is the case with the other proteids. Previous drying of the proteids does not appear to affect the hydrolysis.

J. J. S.

**The Nucleic Acid from the Spermatozoa of *Murænesox cinereus*.** KATSUJI INOUE (*Zeit. physiol. Chem.*, 1906, 48, 181—184. Compare this vol., i, 55).—A nucleic acid has been isolated from the mature spermatozoa of *Murænesox cinereus* Forsk. It appears to contain slightly more nitrogen and phosphorus than the nucleic acid from the intestine. When hydrolysed with 20 per cent. sulphuric acid, it yields lævulic acid, guanine, adenine, xanthine, hypoxanthine, cytosine, and thymine.

J. J. S.

**Preparation and Composition of Myco-nucleic Acids from Yeast.** WILLIAM F. BOOS (*Chem. Centr.*, 1906, i, 1833; from *Arch. exp. Path. Pharm.*, 55, 16—20).—Nucleic acids prepared from yeast by the method adopted by Herlant (*Abstr.*, 1900, i, 466) exhibited variations in the amount of oxygen similar to those observed by Herlant. Four different preparations gave the compositions: (1)  $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2 + 8O$ , (2)  $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2 + 3O$ , (3) and (4)  $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2 + 2H_2O$ . With another method of preparation in which any possible variation in the action of the potassium was avoided, a nucleic acid of the composition  $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2$  was obtained.

T. H. P.

**Latschinoff's Cholocamphoric Acid.** THEODOR PANZER (*Zeit. physiol. Chem.*, 1906, 48, 192—204. Compare Latschinoff, this Journal, 1880, 56, 722).—Cholocamphoric acid, obtained by the oxidation of cholic acid with nitric acid, crystallises from water in long, slender, silky needles and dissolves readily in glacial acetic acid



or in 80 per cent. alcohol. When quickly heated, it turns brown at  $270^{\circ}$  and decomposes at  $286^{\circ}$ . The analytical results agree best with the formula  $C_{14}H_{22}O_6$ , and not the formula  $C_{10}H_{16}O_4$ , suggested by Latschinoff. It appears to be a tribasic acid, but a crystalline anhydride has not been prepared. When the acid is distilled with lime, a benzene hydrocarbon,  $C_{11}H_{16}$ , distilling at  $227^{\circ}$  (uncorr.) is obtained. When the hydrocarbon is oxidised, benzoic and phthalic acids do not appear to be formed, and it is thus probable that in both the hydrocarbon and in the acid at least three side-chains are present. The hydrocarbon is a benzene derivative, and the acid a hexamethylene compound.

J. J. S.

**Diamino-acids derived from Egg-albumin.** LOUIS HUGOUNENQ and J. GALIMARD (*Compt. rend.*, 1906, 143, 242—243).—By hydrolysing egg-albumin with dilute sulphuric acid in presence of sodium chloride, the authors have obtained (1) 2.14 per cent. of arginine; (2) 2.15 per cent. of lysine; (3) a white compound,  $C_{11}H_{18}O_4N_6$ , which crystallises in small needles, soluble in water, but insoluble in alcohol, and is precipitated by acid mercuric sulphate solution; it appears to be a compound of arginine with an acid amide, such as pyrrolidine-2-carboxylic acid; (4) a compound which is not precipitated by mercuric sulphate and yields a hydrochloride,  $C_{10}H_{19}O_6N_5 \cdot 2HCl$ , crystallising in moderately hard, white prisms; this compound is probably a derivative of arginine and aspartic acid. Histidine is absent. T. H. P.

*See errata, V 902<sup>2</sup> p. 1266*

**The True Nature of Lepierre's  $\alpha$ -Glucoproteins.** J. GALIMARD, L. LACOMBE, and ALBERT MOREL (*Compt. rend.*, 1906, 143, 298—300).—The constitution ascribed by Lepierre (*Abstr.*, 1901, i, 622) to the nitrogenous compounds (glucoproteins) which he employed for the cultivation of micro-organisms is inexact; his so-called " $\alpha$ -glucoproteins" are mixtures of monoamino-acids (alanine, leucine, and phenylalanine) containing traces of tyrosine and non-crystalline substances (Hugounenq and Morel, this vol., i, 719), and it is these which play the most important part in the nutrition of the micro-organisms, for the nutritive value of the " $\alpha$ -glucoproteins" is destroyed when all traces of tyrosine and non-crystalline substances are removed by means of repeated crystallisations.

M. A. W.

**Amount of Phosphorus in Egg-albumin.** KARL KAAS (*Monatsh.*, 1906, 27, 403—409. Compare Hofmeister, *Abstr.*, 1898, i, 390; Hopkins and Pinkus, *ibid.*, 456).—The albumin of a fresh hen's egg contained 0.155 per cent., whilst that of an egg one month old contained 0.228 per cent., of phosphorus, the difference being probably in consequence of diffusion of phosphorus from the yolk. Crystalline egg-albumin prepared by Hofmeister and Hopkins's method and Pinkus's method contained 0.919 per cent., but after elimination of the amino-groups by treatment with sodium nitrite and glacial acetic acid, 2.42 per cent., of phosphorus. Of two specimens of pure

egg-albumin, the one prepared by Hofmann and Pinkus' method, and freed from ammonium sulphate by dialysis, contained 0.352 per cent. of phosphorus, whilst the other, prepared by Hammarsten's process, was free from phosphorus. G. Y.

**Animal Gelatins. V. Preparation of Gelatins.** WL. S. SADIKOFF (*Zeit. physiol. Chem.*, 1906, 48, 130—139. Compare Abstr., 1904, i, 125, 126, 462; this vol., i, 224).—The various methods for the preparation and purification of gelatin are discussed. Most of these methods are tedious, remove but part of the impurities, and produce a partial decomposition of the gelatin. The following method is recommended. Pounded bones are extracted with fresh amounts of hydrochloric acid (1:3) for seven to eight days, and then, after washing with water, transferred to a 1—3 per cent. solution of sodium hydroxide. By this method all albumins, mucin, nucleo-proteids, &c., are dissolved, any calcium phosphate is precipitated, and fatty compounds are hydrolysed. After the alkaline liquid has been changed three times, the residue is washed with water and the hyaline mass added to a boiling 1 per cent. solution of chloroacetic acid. The gelatin-yielding substances are readily transformed into gelatin, and after filtration the gelatin may be precipitated by the aid of magnesium sulphate and then washed with water and alcohol.

Gelatin prepared by the ordinary method may be purified by washing with water and then with a cold 20 per cent. aqueous solution of magnesium sulphate. It is then dissolved in warm 20 per cent. magnesium sulphate solution, filtered hot, and to the cold filtrate is added a 0.5 per cent. solution of hydrochloric or sulphuric acid in 20 per cent. magnesium sulphate. The precipitate is removed, washed, dissolved in hot water, and very dilute acid and much alcohol are added, and then the gelatin precipitated by neutralisation with ammonia. J. J. S.

**Absorption of Gallic Acid by Organic Colloids.** WILLIAM P. DREAPER and ALEXANDER WILSON (*J. Soc. Chem. Ind.*, 1906, 25, 515—518).—A detailed account of the experimental results, of which a summary has been published previously (*Proc.*, 1906, 22, 70).

P. H.

**Kyrines.** MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1906, 48, 54—68. Compare Abstr., 1903, i, 586; 1905, i, 104).—Kyrines, the intermediate decomposition products of proteids by acids, are characterised by the constancy of the composition of their sulphates, by the relationship of the nitrogen precipitated by phosphotungstic acid to the total nitrogen, and by their forming characteristic phosphotungstates. Skraup and Zwerger's doubts (this vol., i, 123) as to the homogeneity of caseinokyrine are investigated, and, by following the change in rotation, the hydrolysis of casein at 100° and at 38° is compared. It is possible when mixtures of kyrine sulphate and lysine are precipitated with phosphotungstic acid to distinguish microscopically the mixed phosphotungstates. The picrates also afford a means of distinguishing caseinokyrine from lysine and arginine, the former separating always

as an oil, whereas lysine picrate crystallises immediately the excess of picric acid is removed by ether.

Kyrine obtained from fibrin yields lysine, arginine, and glutamic acid on hydrolysis. Constancy in the composition of the sulphate was obtained after the ninth precipitation; 72.7 per cent. of the nitrogen was then in a form precipitable by phosphotungstic acid and about half the total was in the form of arginine.

E. F. A.

**Hydrolysis of Meat Extract.** KARL MICKO (*Zeit. Nahr. Genussm.*, 1906, 11, 705—729).—The constituents of the mixture obtained on hydrolysing meat extract were separated by Emil Fischer's ester method, alanine, leucine, glycine, and valeric acid being obtained in the earlier fractions. Considerable quantities of lactic acid and of succinic acid were also proved to be present. In all about 20 per cent. of the organic matter of the meat extract was regained in the form of amino-acids. Of these, glutamic acid was present in largest amount; besides those mentioned above, isoleucine and aspartic acid were also isolated. Similar products were obtained on directly esterifying the meat extract.

E. F. A.

**Proteid Reactions attributed to Tryptophan.** FRANZ BARDACHZI (*Zeit. physiol. Chem.*, 1906, 48, 145—159. Compare Hopkins and Cole, *Abstr.*, 1901, i, 310).—The coloured solutions obtained by treating tryptophan with "active" ether and dissolving in hydrochloric acid have been examined by means of a Hüfner spectrophotometer and the light extinction curves drawn. Different solutions give similar curves, but of varying intensity, the variations depending to a certain extent on the amount of ether used.

Solutions obtained by dissolving tryptophan in hydrochloric acid mixed with dilute glyoxylic acid have been examined similarly. When kept, these solutions become paler, but yield practically the same photometric curve. The effect of warming, however, is to force the extinction towards the blue end of the spectrum; but when a further quantity of glyoxylic acid is added to the cooled solution, the original colour and extinction are restored.

Solutions of tryptophan in hydrochloric acid and furfuraldehyde rapidly darken and cannot be examined in the same way.

Various proteids, such as ovalbumin, casein, &c., have been experimented with in the same manner as tryptophan; the clear, coloured solutions are usually obtained on warming only. The colorations are somewhat similar to those given by tryptophan, but the extinction curves are quite different.

The solutions obtained by dissolving cholic acid in fuming hydrochloric acid and furfuraldehyde and in hydrochloric acid and sucrose (2 per cent.) give curves which do not resemble one another.

J. J. S.

**Photographic Determination of the Absorption Bands of the Colouring Matters of Blood.** LOUIS LEWIN, A. MIETHE, and E. STENGER (*Compt. rend.*, 1906, 143, 115—117).—The absorption spectra of blood, of hæmoglobin, and of some of its derivatives have



been photographed and measured in terms of wave-lengths. From a large number of experiments with solutions of different concentrations, the most suitable dilution for the measurement of a particular band has been determined. The detailed results are summarised in a table. It appears that the absorption bands in the less refrangible part of the spectrum are in general less characteristic than those in the more refrangible portion.

H. M. D.

**Formation of Methæmoglobin.** I. ALLEXIS BABEL (*Arch. Sci. phys. nat.*, 1906, [iv], 22, 146—162).—The author has examined, spectroscopically, the action on pig's blood of a number of simple organic compounds, such as aniline and phenol and their principal derivatives, in order to determine their relative capacities for converting oxyhæmoglobin into methæmoglobin. Numbers are given expressing the minimum quantities in grams of the various substances required to produce an absorption band of a certain intensity when allowed to act for three hours at 20° on 20 c.c. of blood diluted to a concentration of about 5 per cent.

The methæmoglobinising activities of the substances examined are analogous to their chemical reactivities. All causes tending to render the molecule of a compound more stable, and so to diminish its capability of combination, exert influences in the same sense on the formation of methæmoglobin. Thus, the introduction of a sulphonic or carboxyl group into a molecule renders it much more resistant to the action of reagents; the sulphanilates and anthranilates have also much less marked hæmoglobinising actions than aniline, from which they are derived.

T. H. P.

**Action of Sodium Fluoride on Methæmoglobins obtained from Globin and Hæmatin.** JOSEPH MOITESSIER (*Bull. Soc. chim.*, 1906, [iii], 35, 575—576).—The author has investigated the optical effect produced by the addition of sodium fluoride to solutions of methæmoglobins synthesised from globin and hæmatin from various sources (Bertin Sans and Moitessier, *Abstr.*, 1894, i, 216), and finds that the absorption bands are intensified and displaced as recorded by Ville and Derrien (*Abstr.*, 1905, i, 399, 500).

T. A. H.

**Colouring Matter of Blood.** VI. JOZEF BURACZEWSKI and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1906, 47, 331—334. Compare *Abstr.*, 1905, i, 399).—The product obtained by distilling  $\alpha$ -methyl- $\beta$ -propylmaleimide with zinc dust in an atmosphere of hydrogen condenses with diazobenzene chloride, yielding an azo-dye, the optical properties of which resemble those of the hæmopyrrolebisazo-dye. But although the hydrochloride of the latter crystallises readily, the hydrochloride of the dye from the synthetical product has not been obtained so far in a crystalline form.

J. J. S.

**Specific Action of Peroxydases.** ROBERT CHODAT (*Ber.*, 1906, 39, 2506—2507).—A claim for priority on behalf of Chodat and Bach as against Bach (this vol., i, 616).

G. Y.

**Hydrolytic Activity of Liver Histozyms and Enzymes on some Glucosides and Alkaloids.** MAX GONNERMANN (*Pflüger's Archiv*, 1906, 113, 168—197).—The action of the extract of the liver of the ox, hare, dog, horse, and fish, and a number of enzymes also of some bacilli has been investigated, using the glucosides sinigrin, arbutin, amygdalin, sapotoxin, and the alkaloids atropine, cocaine, morphine, and hydroxydimorphine as test materials. In no instance is sinigrin affected, showing the rarity of the occurrence of myrosin. Arbutin is hydrolysed by the liver extracts, by emulsin, by some bacilli, and by tyrosinase. Amygdalin is affected by the liver extracts of the ox and hare alone, also by trypsin, emulsin, and some bacilli, whilst it is hydrolysed within twenty-four hours by tyrosinase. Sapotoxin is hydrolysed by liver extracts and also by emulsin and tyrosinase. Atropine is attacked by the liver enzymes, also by pancreatin, by trypsin, and by tyrosinase. Cocaine by the histozyms, by pancreatin, trypsin, and emulsin, and by bacilli, but not by pepsin, maltase, or invertase. Morphine is only positively attacked by tyrosinase, and partially, perhaps, by the liver histozyms of the hare and the dog. All the enzymes were without action on hydroxydimorphine.

E. F. A.

**Effect of Heat on Enzyme Activity.** WILHELM CRAMER and A. R. BEARN (*Proc. Physiol. Soc.*, 1906, xxxvi—xxxvii; *J. Physiol.*, 34).—Experiments with pepsin and rennin show that the presence of the enzyme inactivated by heating to 56—60° hinders, or in sufficient amount completely inhibits, the action of the active enzyme. Heating to 100° weakens or destroys their power. If enzyme action consists of the stages (1) the formation of a compound between substrate and enzyme, and (2) the breaking down of this compound, then the above results are explicable as follows: heating to 60° has not affected the first stage; the substrate which has combined with the inactivated enzyme cannot therefore take up the active enzyme, and is thus protected from its action. Heating to 100° changes the structure of the enzyme so profoundly that it can no longer combine with the substrate.

W. D. H.

**Enzymes in Relation to Concentrated Electric Light.** SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1906, 8, 481—483. Compare Abstr., 1905, ii, 48).—Concentrated electric light inactivates chymosin (rennin) to a very considerable extent. The same is true for its zymogen and for the anti-rennin of blood-serum.

W. D. H.

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## Organic Chemistry.

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**Acetyl Chloride and Hydrochloric Acid as Reagents for distinguishing between the Various Types of Monohydric Alcohols.** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 261—280).—Acetyl chloride reacts with primary or secondary alcohols, converting them quantitatively into esters of acetic acid (with evolution of hydrogen chloride), whereas tertiary alcohols under the same conditions are converted into chlorides.

These two reactions were found to take place concurrently and independently of each other when mixtures of tertiary with primary or secondary alcohols were treated with acetyl chloride.

Tertiary alcohols, except those of very high molecular weight, dissolve at once in fuming hydrochloric acid; the solution rapidly becomes turbid owing to the formation of the chloride, which rises to the surface as an oil. This change takes place in the cold, although the reaction is facilitated by warming gently. Primary or secondary alcohols, on the other hand, also dissolve in fuming hydrochloric acid, and two layers are again formed after a time, but the upper one in this case consists only of the unchanged alcohol saturated with hydrogen chloride, no esterification taking place unless the mixture is warmed.

P. H.

**Application of the Principle of Partition. VI. Action of Hydrogen chloride on Propylene Oxide and Propenyl Alcohol.** ARTHUR MICHAEL (*Ber.*, 1906, 39, 2785—2789. Compare this vol., i, 620).—By the action of dry hydrogen chloride in the cold on propylene oxide, a chlorohydrin is formed, which boils at 127—127·5° (corr.) under 722 mm. pressure and has a sp. gr. 1·113 at 20°/20°; allyl chloride yields a chlorohydrin, boiling at 126—126·5° (corr.) under 722 mm. pressure, and having a sp. gr. 1·115 at 20°/20°. The compound is probably therefore  $\omega$ -chloroisopropyl alcohol,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ , containing a small quantity of  $\beta$ -chloropropyl alcohol. The chlorohydrin from propenyl alcohol boiled at 127—127·5°, and had a sp. gr. 1·112 at 20°/20°; it also consisted mainly of  $\omega$ -chloroisopropyl alcohol.

E. F. A.

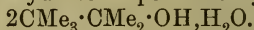
**Application of the Principle of Partition. VII. Action of Hydrogen Chloride on *iso*Butylene Oxide.** ARTHUR MICHAEL and VIRGIL L. LEIGHTON (*Ber.*, 1906, 39, 2789—2795. Compare preceding abstract).—By the action of dry hydrogen chloride on *isobutylene* oxide, an *isobutylene* chlorohydrin is obtained, which boils at 127—130°, and has a sp. gr. 1·0587 at 20°/20°, whereas the product  $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{OH}$ , obtained by the addition of hypochlorous acid to *isobutylene*, boils at 128—129° and has a sp. gr. 1·0663 at 20°/20°. The *isobutylene* chlorohydrin when warmed with aqueous sodium carbonate or potassium acetate forms *isobutaldehyde*, and behaves, in fact, as if it were a mixture of one



part of  $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$  and two parts of  $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{OH}$ , a supposition confirmed by decomposition with phosphoric oxide, when a mixture of isomeric chloroisobutylenes is obtained two-thirds as great as if obtained from  $\beta$ -chloroisobutyl alcohol.

E. F. A.

**New Syntheses of Pentamethylethanol and of Hexamethylethane.** LOUIS HENRY [with AUG. DE WAEL] (*Bull. Acad. roy. Belg.*, 1906, 352—363. Compare this vol., i, 477).—Pentamethylethanol may be prepared either by the action of magnesium methyl bromide on pinacolin or by the action of acetone on *tert.*-butyl chloride and magnesium. Hexamethylethane is obtained by acting on magnesium methyl bromide with an ethereal solution of bromopentamethylethane; the latter substance was prepared by passing hydrogen bromide into an alcoholic solution of the hydrate of pentamethylethanol,

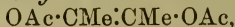


*Bromopentamethylethane*,  $\text{CMe}_3\cdot\text{CMe}_2\text{Br}$ , is a white solid which gradually becomes faintly yellow; it melts and partially decomposes in a sealed capillary tube at  $143^\circ$ . When heated in an open tube it volatilises; the substance has an odour of camphor, is very slightly soluble in alcohol, but dissolves readily in ether.

P. H.

**Action of Sodium on Esters of Fatty Acids. Preparation of Acyloins of the Type  $\text{R}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{R}$ . Mechanism of the Reaction.** LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 629—633, 633—636).—The first paper gives a general account of work already dealt with in Abstr., 1903, i, 597, 673, 730; 1904, i, 213, 642; 1905, i, 11, 12, 13, 560, and suggests the general name "acyloins" for the hydroxyketones of the type  $\text{R}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{R}$  produced in this reaction.

The yellow sodium derivative, eventually precipitated when ethyl acetate is treated with sodium by the general method already described (Abstr., 1905, i, 560), is converted by acetyl chloride into acetyl-methylcarbonyl acetate,  $\text{CMe}\cdot\text{CHMe}\cdot\text{OAc}$  (van Reymenant, Abstr., 1901, i, 126), and the *diacetyl* derivative of *butene-2:3-diol*,



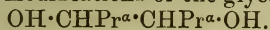
which has a sp. gr.  $0.950$  at  $0^\circ/4^\circ$  and boils at  $110$ — $115^\circ$  under 29 mm. pressure. The former is produced by partial hydrolysis of the latter. From these reactions it appears that the yellow sodium derivative must have the constitution  $\text{ONa}\cdot\text{CMe}:\text{CMe}\cdot\text{ONa}$ , and that the formation of acyloins from esters takes place in the following steps:  $2(\text{R}\cdot\text{CO}_2\text{Et}) \rightarrow \text{ONa}\cdot\text{CR}:\text{CR}\cdot\text{ONa} \rightarrow \text{OH}\cdot\text{CR}:\text{CR}\cdot\text{OH} \rightarrow \text{R}\cdot\text{CO}\cdot\text{CHR}\cdot\text{OH}$ .

T. A. H.

**Acyloins of the Fatty Series. III and IV.** LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 637—641, 641—643. Compare Abstr., 1905, i, 560, 572, and preceding abstract).—Propioin,  $\text{COEt}\cdot\text{CHEt}\cdot\text{OH}$ , boils at  $72$ — $73^\circ$  under 20 mm. pressure, has sp. gr.  $0.968$  at  $0^\circ/4^\circ$ , and polymerises slightly when distilled at atmospheric pressure (compare Anderlini, Abstr., 1896, i, 202). The *acetyl* derivative has a sp. gr.  $1.001$  at  $0^\circ/4^\circ$  and boils at  $85$ — $96^\circ$  under

17 mm. pressure. The *semicarbazone* forms small crystals, melts at  $137^{\circ}$ , and is readily soluble in water.

Butyroin,  $\text{COPr}^{\alpha}\cdot\text{CHPr}^{\alpha}\cdot\text{OH}$ , boils at  $85^{\circ}$  under 10 mm. pressure (compare Klinger and Schmitz, Abstr., 1891, 890). Its oxime (Abstr., 1905, i, 572, and Münchmeyer, Abstr., 1886, 350), when heated with acetic anhydride, decomposes into butyraldehyde and propyl cyanide. The *acetyl* derivative has a sp. gr. 0.9807 at  $0^{\circ}/4^{\circ}$  and boils at  $117\text{--}118^{\circ}$  under 21 mm. pressure. When butyroin is heated with potassium hydroxide in water, the principal product is a mixture of the two stereoisomeric modifications of the glycol,



The dipropylglycollic acid which Klinger and Schmitz obtained from their butyroin in this reaction was probably formed by the action of the alkali on some dibutyryl present in the butyroin used. A mixture of butyroin and pyruvic acid when heated yields butyroin pyruvate and a liquid having the properties of 4-octanone. The former forms with semicarbazide a substance having the composition of a semicarbazone, less 1 mol. of water (compare Abstr., 1905, i, 572). Butyroin on heating with sulphuric acid yields *dibutyroin*,  $\text{C}_{16}\text{H}_{28}\text{O}_2$ , which is liquid, has sp. gr. 0.939, and boils at  $155\text{--}157^{\circ}$  under 12 mm. pressure.

*iso*Butyroin,  $\text{COPr}^{\beta}\cdot\text{CHPr}^{\beta}\cdot\text{OH}$ , has sp. gr. 0.931 and boils at  $83^{\circ}$  under 26 mm. pressure (compare Klinger and Basse, *loc. cit.*). The *oxime* melts at  $110\text{--}111^{\circ}$  and boils at  $137^{\circ}$  under 14 mm. pressure; a semicarbazone could not be obtained.

*Hexonoin*,  $\text{C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{C}_5\text{H}_{11}$ , has a sp. gr. 0.910 at  $0^{\circ}/4^{\circ}$ , boils at  $130\text{--}132^{\circ}$  under 8 mm. pressure, and when dehydrated by sulphuric acid yields dihexonoin, which boils at  $225\text{--}230^{\circ}$  under 10 mm. pressure (compare Abstr., 1905, i, 561, 573).

*Pivaloin*,  $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CMe}_3$ , prepared by the general method from methyl pivalate, crystallises from ether in small needles, melts and sublimes at  $81^{\circ}$ , and is very stable. Like *isobutyroin* it does not yield a semicarbazone.

T. A. H.

**Hydrogenation of Fatty Acyloins.** Preparation of *s*-Disubstituted Glycols, Alcohols of the Type  $\text{OH}\cdot\text{CHR}\cdot\text{CH}_2\text{R}$ , and the Corresponding Ketones. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 643—646, 646—650. Compare preceding abstracts).—The reduction is effected by allowing an alcoholic solution of the acyloin to drop slowly into a flask containing large fragments of sodium. The products of the action are (1) a mixture of the two stereoisomeric modifications of the symmetric disubstituted glycol of the type  $\text{OH}\cdot\text{CHR}\cdot\text{CHR}\cdot\text{OH}$ , and (2) a secondary alcohol of the type  $\text{CH}_2\text{R}\cdot\text{CHR}\cdot\text{OH}$ , the former being always produced in the larger quantity. Since both these reduction products are readily convertible into ketones of the type  $\text{RCO}\cdot\text{CH}_2\text{R}$ , the former by heating with dilute sulphuric acid at  $180^{\circ}$  in closed vessels and the latter by oxidation with chromic acid, these reactions furnish a means of converting acyloins almost quantitatively into these ketones, which the authors suggest might be called homoacylones, the symmetrical ketones,  $\text{R}\cdot\text{CO}\cdot\text{R}$ , being known as acylones. The products obtained from

butyrolin and hexonoin by these reactions are described in Abstr., 1905, i, 573.

When the mixture of the two stereoisomeric dodecane- $\zeta\eta$ -diols are treated with phosphorus chloride or bromide, they furnish the two corresponding stereoisomeric halogen derivatives. The mixture of dichloro-derivatives boils at 115—135° under 10 mm. pressure and is scarcely affected by zinc dust in presence of alcohol, but the mixture of the dibromo-derivatives, similarly obtained, which boils at 145° under 10 mm. pressure, is readily reduced to dodecylene,



The purest specimen of this obtained contained from 25 to 30 per cent. of a saturated hydrocarbon and boiled at 208—209°. T. A. H.

“Steric Hindrance” in Derivatives of Pivaloin. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 655—657).—Whilst the normal acyloins condense readily with semicarbazide, *isobutyrolin* does so only with difficulty (this vol., i, 783). Further, whilst hydroxylamine readily gives dioximes with the normal  $\alpha$ -diketones, it reacts much less readily with *diisobutyryl*. These observations indicate that the reactivity of a carbonyl group is lessened by the multiplication of methyl groups in its vicinity. This influence is at its maximum in pivaloin,  $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CMe}_3$ , which does not form a semicarbazone (this vol., i, 783). Further, on reduction with sodium and alcohol it does not yield the corresponding glycol, but only the *monohydric alcohol*,  $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CMe}_3$ , which separates from light petroleum in splendid crystals, melts at 52—53°, boils at 173—174°, sublimes readily, and is volatile in a current of steam. On oxidation with chromic acid in presence of sulphuric acid, it yields *homopivalone*,  $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}_3$ , an unpleasant-smelling liquid, which has a sp. gr. 0.827 at 0°/4° and boils at 163°. Even when heated with hydroxylamine hydrochloride and zinc oxide for seven hours, this ketone furnishes no oxime and similarly it yields no semicarbazone.

*Dipivaloyl*,  $\text{CMe}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CMe}_3$ , obtained by dehydrogenating pivaloin by Sabatier and Senderens' method, is a yellow liquid, has sp. gr. 0.895 at 0°/4°, and boils at 70° under 21 mm. and at 169—170° under atmospheric pressure. When heated with hydroxylamine hydrochloride and zinc oxide in great excess for twenty-four hours, it yields about 30 per cent. of the *monoxime*, which separates from light petroleum in slender needles and melts at 123°. T. A. H.

*tert.*-Pinacolyl Alcohol. MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1906, 281—287).—The alcohol obtained by the action of acetone on *isopropyl bromide* and magnesium boils at 118.8—119.6° and still remains liquid at -15°, whereas the substance obtained by the reduction of pinacolin boils at 120.2—120.6° and melts at +3.6°; the synthetic compound is also more mobile. P. H.

Preparation of  $\gamma$ -,  $\delta$ -,  $\epsilon$ -, &c., Glycols and their Derivatives from the Corresponding Lactones. FRIEDRICH W. SEMMLER (*Ber.*, 1906, 39, 2851—2857).—Good yields of  $\gamma$ -,  $\delta$ -, &c., glycols are

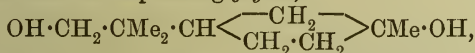


readily obtained by reducing the corresponding lactones with sodium and boiling alcohol. The following glycols have been prepared by this method. Pentane- $\alpha\delta$ -diol from  $\gamma$ -valerolactone; a by-product is hydroxyvaleric acid. A glycol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}(\text{CH}_2\cdot\text{OH})\\ \text{CH}_2\text{---CH}_2\end{smallmatrix}\right\rangle\text{CHMe}$  or

$\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}(\text{CH}_2\cdot\text{OH})\\ \text{CH}_2\text{---CH}_2\end{smallmatrix}\right\rangle\text{CHMe}$ , from the lactone of pulegenic acid; it distils at  $137\text{--}140^\circ$  under 10 mm. pressure, and has  $n_D$  1.4715 and a sp. gr. 0.9945 at  $20^\circ$ . With concentrated sulphuric acid, it yields an oxide,  $\text{C}_{10}\text{H}_{18}\text{O}$ .  $\beta\zeta$ -Dimethyloctane- $\gamma\theta$ -diol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$ , boiling at  $147^\circ$  under 10 mm. pressure, from the lactone of  $\epsilon$ -hydroxy- $\beta\zeta$ -dimethyloctoic acid (Baeyer, Abstr., 1900, i, 329).

*o*-Hydroxydihydrocinnamyl alcohol,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , a liquid distilling at  $177\text{--}178^\circ$  under 8 mm. pressure and having a sp. gr. 1.1293 at  $20^\circ$  and  $n_D$  1.55984, is prepared from coumarin. Its benzoyl derivative melts at  $99\text{--}100^\circ$ , and with sulphuric acid the alcohol gives a good yield of chroman (Abstr., 1905, i, 294).

The compound obtained by Czerny (Abstr., 1900, i, 675) by the action of concentrated sulphuric acid on  $\alpha$ -fencholenic acid (Cockburn, Trans., 1899, 75, 506) is the lactone of  $\alpha$ -fencholenic acid, and on reduction yields the corresponding glycol,



which boils at  $158\text{--}161^\circ$  under 11 mm. pressure. With sulphuric acid, it yields an oxide, which is identical with Wallach's fenchol (Abstr., 1895, i, 381).

The lactone of  $\beta$ -fencholenic acid,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , boils at  $116\text{--}118^\circ$  under 8 mm. pressure, has a sp. gr. 1.0343 at  $25^\circ$ , and when reduced yields the glycol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2\\ \text{---CH}_2\end{smallmatrix}\right\rangle\text{CMe}\cdot\text{CH}_2\cdot\text{OH}$ , boiling at  $142\text{--}143^\circ$  under 8—9 mm. pressure.

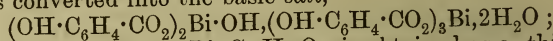
J. J. S.

**Action of the Polyhydric Alcohols on Bismuth Salts and the Preparation of Bismuth Salts by means of a Solution of Mannitol Bismuth Nitrate.** LUDWIG VANINO and F. HARTL (*J. pr. Chem.*, 1906, [ii], 74, 142—152. Compare Vanino and Hauser, Abstr., 1902, i, 8).—On addition of much acetone to an aqueous solution of mannitol bismuth nitrate, there is formed a hard crystalline compound,  $2\text{Bi}(\text{NO}_3)_3\cdot\text{C}_6\text{H}_{14}\text{O}_6$ , which is very soluble in water. Sorbitol and dulcitol behave towards bismuth nitrate in the same manner as does mannitol. The white, crystalline precipitate,  $\text{Bi}(\text{NO}_3)_3\cdot\text{C}_6\text{H}_{14}\text{O}_6$ , obtained on addition of acetone to the sorbitol bismuth nitrate solution, is readily soluble in water; the similar precipitate obtained from the dulcitol bismuth nitrate solution has the composition  $\text{BiO}\cdot\text{NO}_3\cdot\text{C}_6\text{H}_{14}\text{O}_6$ . In aqueous solution these three substances give a blackish-brown coloration with hydrogen sulphide, do not form precipitates with potassium hydroxide, and yield bismuth oxyiodide on addition of potassium iodide.

The following salts of bismuth are prepared by adding the corresponding free acids or the sodium salts to the aqueous solution of

bismuth nitrate and mannitol; a precipitate is not formed on addition of nitric acid or sodium nitrate.

*Bismuth salicylate*,  $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2)_3\text{Bi} \cdot 2\text{H}_2\text{O}$ , forms a thick, white, crystalline meal, is sparingly soluble in alcohol, and on prolonged washing is converted into the basic salt,



the *camphorate*,  $(\text{C}_{10}\text{H}_{14}\text{O}_4)_3\text{Bi}_2 \cdot \text{C}_{10}\text{H}_{16}\text{O}_4$ , is obtained as a thick, white, crystalline meal; *phthalate*,  $(\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2)_3\text{Bi}$ , crystallises in white, quadratic plates, and is not decomposed by potassium hydroxide; *citrate*,  $\text{OH} \cdot \text{C}_3\text{H}_4(\text{CO}_2)_3\text{Bi}$ , forms a white, crystalline precipitate; *benzoate*,  $(\text{C}_6\text{H}_5 \cdot \text{CO}_2)_3\text{Bi}$ , crystallises in white needles; *oxalate*,  $(\text{C}_2\text{O}_4)_3\text{Bi}_2 \cdot \text{H}_2\text{O}$ , forms a white, micro-crystalline precipitate; *nitrite*,  $\text{BiO} \cdot \text{NO} \cdot \frac{1}{2}\text{H}_2\text{O}$ , is obtained as a yellowish-white precipitate, which decomposes above  $60^\circ$  and dissolves readily in hydrochloric acid, forming a solution remaining clear on dilution; *hypophosphite*,  $\text{Bi}(\text{H}_2\text{PO}_2)_3$ , forms a white, crystalline precipitate, which decomposes slowly when dry, more quickly when moist, with separation of metallic bismuth; *phosphite*,  $\text{Bi}_2(\text{HPO}_3)_3 \cdot 3\text{H}_2\text{O}$ , crystallises in white, tetragonal needles and is not decomposed by potassium hydroxide; *phosphate*,  $\text{BiPO}_4 \cdot 3\text{H}_2\text{O}$ , forms a white, gelatinous precipitate; *borate*,  $\text{BiBO}_3 \cdot 2\text{H}_2\text{O}$ , is obtained as a white, fine-granular precipitate, and does not react with potassium hydroxide or iodide; *ferrocyanide*,  $\text{Bi}_4[\text{Fe}(\text{CN})_6]_3 \cdot 2\text{K}_4\text{Fe}(\text{CN})_6$ , forms a yellow, amorphous precipitate, which becomes green and crystalline when dried, and does not react with potassium hydroxide or iodide.

With the exceptions mentioned, these bismuth salts are blackened by hydrogen sulphide and are decomposed by potassium hydroxide and iodide. G. Y.

**Compounds of Mercuric Chloride and Alcohols with Dicyclopentadiene.** KARL A. HOFMANN and E. SEILER (*Ber.*, 1906, 39, 3187—3190. Compare Hofmann and Sand, *Abstr.*, 1900, i, 384).—The authors have investigated the action of mercuric chloride on alcoholic solutions of dicyclopentadiene.

The compound  $\text{HgCl}_2 \cdot \text{C}_{10}\text{H}_{12} \cdot \text{OMe}$ , prepared from mercuric chloride, methyl alcohol, and dicyclopentadiene, separates from a mixture of methyl alcohol and water in faintly yellow needles and melts at  $133^\circ$ . When acted on by hydrochloric acid, it regenerates dicyclopentadiene. When its solution in concentrated sulphuric acid is warmed, it assumes a pink coloration with a green fluorescence.

The compound  $\text{HgCl}_2 \cdot \text{C}_{10}\text{H}_{12} \cdot \text{OEt}$ , prepared from mercuric chloride, ethyl alcohol, and dicyclopentadiene, crystallises from aqueous alcohol in prisms and melts at  $98^\circ$ . From the stability of the compound on long exposure under diminished pressure and also at  $90^\circ$ , as well as from the cryoscopic determinations made in benzene solution, it is deduced that the alcohol is not present in the molecule as alcohol of crystallisation. The presence of an unsaturated linking in the molecule is shown by the behaviour of the compound towards permanganate.

The compound  $\text{HgCl}_2 \cdot \text{C}_{10}\text{H}_{12} \cdot \text{O} \cdot \text{C}_5\text{H}_{11}$ , obtained from amyl alcohol, mercuric chloride, and dicyclopentadiene, is a heavy oil and solidifies at about  $-12^\circ$ . A. McK,

**Action of Hydrogen Bromide on Primary and Secondary Saturated Alcohols.** H. FOURNIER (*Bull. Soc. chim.*, 1906, [iii], 35, 621—625).—A regular current of hydrogen bromide may be obtained by allowing bromine to fall, drop by drop, into toluene containing 2 per cent. of its weight of steel wire. The hydrogen bromide so produced is passed through a reflux condenser, then through a U-tube containing yellow phosphorus and a little water, and finally into the appropriate alcohol contained in a flask fitted with a Vigreux column, leading to a condenser. The alcohol is at first heated to within a few degrees of its boiling point, and eventually to such a temperature that the alkyl bromide produced will just distil. The yield is always about 70 per cent.

The following alcohols have been converted into the corresponding alkyl bromides by the above method: ethyl, propyl, isopropyl, isobutyl, *n*-butyl, *n*-amyl, isoamyl, and isohexyl. The last four alcohols were prepared by Grignard and Tissier's method (*Abstr.*, 1902, i, 198).  
T. A. H.

**Organic Nitrates.** PETER KLASON and TOR CARLSON (*Ber.*, 1906, 39, 2752—2754).—Assuming the peroxide formula,  $\text{OEt}\cdot\text{O}\cdot\text{NO}$ , for ethyl nitrate (Baeyer and Villiger, *Ber.*, 1901, 34, 755; Brühl, *Abstr.*, 1898, ii, 362), the formation of alkali nitrate and nitrite on hydrolysis can be accounted for by means of the following reactions:  $\text{OEt}\cdot\text{O}\cdot\text{NO} + \text{KOH} = \text{KO}\cdot\text{O}\cdot\text{NO} + \text{EtOH}$  and  $\text{OEt}\cdot\text{O}\cdot\text{NO} + \text{KOH} = \text{KO}\cdot\text{NO} + \text{OEt}\cdot\text{OH}$ .

The probable formation of an alkyl peroxide has been shown by conducting the hydrolysis in the presence of phenyl hydrosulphide, when an appreciable amount of phenyl disulphide is formed, as would be expected from the equation  $\text{RO}\cdot\text{OH} + 2\text{R}'\cdot\text{SH} = \text{R}\cdot\text{OH} + \text{R}'_2\text{S}_2 + \text{H}_2\text{O}$ . The formation of the disulphide has been proved with glyceryl trinitrate, cellulose nitrate and ethyl nitrate.  
J. J. S.

**Crystalline Form of Platinichlorides of Sulphine Derivatives.** GREGORI AMINOFF (*Zeit. Kryst. Min.*, 1906, 42, 379—383).—Crystallographic details are given respecting several substances prepared by D. Strömholm (*Abstr.*, 1900, i, 325).  
L. J. S.

**Preparation of the Chloride of Methionie Acid.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 171935).—Although, as shown by Kohler (*Abstr.*, 1898, i, 68), the action of phosphorus pentachloride on potassium methionate leads to the production of chloromethanesulphonic chloride, yet it has now been found that methionyl chloride may be prepared by treating free methionie acid with the chlorides or oxychloride of phosphorus. The dry acid (100 parts) is gently warmed with 240 parts of phosphorus pentachloride, the oxychloride distilled off, and the residue fractionated under diminished pressure. *Methionyl chloride*,  $\text{CH}_2(\text{SO}_2\text{Cl})_2$ , is a colourless liquid boiling at  $135^\circ$  under 10 mm. pressure; it is slowly hydrolysed by water, and with aniline in chloroform solution it yields the *anilide*,  $\text{CH}_2(\text{SO}_2\cdot\text{NHPh})_2$ ; this is sparingly soluble in water, but dissolves in dilute aqueous alkalis, being reprecipitated by acids. G. T. M.



**Constitution of Paris Green and its Homologues.** SAMUEL AVERY (*J. Amer. Chem. Soc.*, 1906, 28, 1155—1164).—A large number of specimens of Paris green prepared in several different ways, with an excess of copper, excess of acetic acid, excess of ammonia, or with an excess of any two of these, were analysed and found to contain between 57·3 and 57·7 per cent. of arsenious oxide [ $3\text{CuAs}_2\text{O}_4, \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  requires  $\text{As}_2\text{O}_3 = 58·55$  per cent.]. The formic, propionic, and butyric homologues were also prepared and analysed. The results show that these substances are compounds of copper meta-arsenite and a copper salt of the organic acid combined in a ratio which is usually nearly 3:1, but sometimes approaches 2:1. Between these limits, the crystalline structure and colour do not vary with the composition. Efforts were made to obtain compounds of a ratio 4:1 and 1:1 but without success. It was found that in a series of organic acids, the stronger the acid, the more nearly does the ratio approach 3:1. Thus the formic acid compound is more nearly of this composition than the acetic acid compound, and the latter more so than the propionic homologue. A similar green compound can be obtained with succinic acid, and, in general, such compounds may be formed whenever an acid containing a carboxyl group yields a soluble copper salt and does not form complex ions with copper.

When Paris green of composition approximately 3:1 is boiled with a large excess of solution of arsenious oxide, a product of more exactly 3:1 composition is obtained, but the amount of arsenic never quite reaches that required by the formula  $3\text{CuAs}_2\text{O}_4, \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ . If the boiling is continued, the substance suddenly becomes paler in colour and is converted into anhydrous copper meta-arsenite. By treating Paris green with neutral copper acetate solution, a brown, amorphous powder is obtained which contains a larger proportion of copper than Paris green and is always hydrated. When Paris green is boiled for several hours with water, it is gradually resolved into its components.

On the addition of arsenious oxide solution to a solution of zinc acetate containing a little free acetic acid, a white, granular precipitate is obtained which appears to consist of zinc meta-arsenite crystallised with a small quantity of zinc acetate. The preparation of *zinc meta-arsenite* is described. When zinc butyrate is substituted for the acetate, the precipitate obtained on adding arsenious oxide may contain as much as 10 per cent. of butyric anhydride, but in this case the precipitate contains a considerable quantity of zinc ortho-arsenite. It is evident, therefore, that the stronger acid has a greater tendency to replace arsenious acid in the zinc compounds as well as in those of copper.

E. G.

**Action of Alkali Carbonates on  $\beta\gamma$ -Dibromo-*aa*-dimethyl Acids. Part I.** ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 657—664).— $\beta\gamma$ -Dibromo-*aa*-dimethylbutyric acid is not reduced by zinc and acetic acid, but is reconverted into *aa*-dimethylvinylacetic acid (this vol., i, 231). On treatment with a dilute aqueous solution of potassium carbonate, it yields  $\beta$ -bromo-*aa*-dimethylbutyrolactone,

$\begin{array}{c} \text{CHBr} \cdot \text{CMe}_2 \\ | \\ \text{CH}_2 - \text{O} \end{array} > \text{CO}$ , which crystallises from light petroleum in groups of colourless needles, melts at  $47^\circ$ , and when boiled for two hours with an aqueous solution of potassium carbonate (2 mols.) gives off carbon dioxide and yields *dimethylallyl alcohol*,  $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$ , and  *$\beta$ -hydroxy- $\alpha$ -dimethylbutyrolactone*. The latter crystallises in hygroscopic needles, melts at  $31^\circ$ , and boils at  $163^\circ$  under 15 mm. pressure. The formation of dimethylallyl alcohol in this reaction is assumed to take place in the following way:  $\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CHMe}_2 \rightarrow \text{OH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CMe}_2$ . The alcohol is a sweet-smelling, mobile liquid, which boils at  $65^\circ$  under 24 mm. or at  $140^\circ$  under atmospheric pressure; the *acetate* is a liquid of pleasant odour and boils at  $152^\circ$ ; the *phenylcarbamate* crystallises from a mixture of ether and light petroleum in colourless needles and melts at  $65^\circ$ . On bromination, dimethylallyl alcohol yields  *$\alpha\beta$ -dibromo- $\beta$ -methylbutyl alcohol*, which crystallises from light petroleum in colourless needles and melts at  $37\text{--}38^\circ$ . On oxidation with permanganate, dimethylallyl alcohol yields acetone and oxalic acid.

When  *$\beta$ -bromo- $\alpha$ -dimethylvalerolactone* is boiled with an aqueous solution of potassium carbonate (2 mols.), the products formed are the *methylpentenol*,  $\text{CMe}_2 \cdot \text{CH} \cdot \text{CHMe} \cdot \text{OH}$ , an odorous liquid, which boils at  $65^\circ$  under 38 mm. pressure, and  *$\beta$ -hydroxy- $\alpha$ -dimethylvalerolactone*. The latter, which is the principal product of the reaction, separates from light petroleum in opaque crystals and melts at  $80^\circ$ .

The two  *$\beta\gamma$ -dibromo- $\alpha$ -dimethyl acids* dealt with in the present paper belong to the type  $\text{R} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , where R may be an alkyl radicle or a hydrogen atom. The acids of the type  $\text{CH}_2\text{Br} \cdot \text{CRBr} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , where R may be aliphatic or aromatic, on treatment with alkali carbonates yield a tertiary alcohol, which undergoes dehydration, so that the final product of the reaction is a diethylenic hydrocarbon. It is suggested that this reaction takes place in the following steps:  $\text{CH}_2\text{Br} \cdot \text{CMeBr} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{CH}_2\text{Br} \cdot \text{CMe}(\text{CO}_2\text{H}) \cdot \text{CMe}_2\text{Br} \rightarrow \text{CH}_2\text{Br} \cdot \text{CHMe} \cdot \text{CMe}_2\text{Br} \rightarrow \text{CH}_2 \cdot \text{CMe} \cdot \text{CMe}_2\text{Br} \rightarrow \text{CH}_2 \cdot \text{CMe} \cdot \text{CMe}_2 \cdot \text{OH} \rightarrow \text{CH}_2 \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CH}_2$ .

The migration of a carboxyl group, which is assumed here, has been observed to occur in the action of phosphoric oxide on phenyl-hydroxypivalic acid.

T. A. H.

**Reaction between Silver Nitrate and Organic Halogen Compounds.** HANS EULER (*Ber.*, 1906, 39, 2726—2734. Compare J. Wislicenus, *Abstr.*, 1882, 934; Hecht, Conrad, and Brückner, *ibid.*, 1890, 4; Wildermann, 1892, 399; Lobry de Bruyn and Steger, 1899, i, 744, 745, 849; Burke and Donnan, *Trans.*, 1904, 85, 555). —The reaction between monochloroacetic acid and silver nitrate,  $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H} + \text{AgNO}_3 + \text{H}_2\text{O} = \text{AgCl} + \text{OH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} + \text{HNO}_3$ , in both aqueous and 45 per cent. alcoholic solution, is bimolecular, and the value of *K* for both solvents at  $80^\circ$  is 0.0018. The constant decreases to a slight extent as the time increases, and this is due to the formation of free nitric acid. The temperature-coefficient is relatively high, as indicated by the following numbers: 1000 *K*, 0.45 at  $65^\circ$ , 0.70 at  $70^\circ$ , and 1.80 at  $80^\circ$ .

The constant for the reaction between ethyl chloroacetate and silver nitrate in 45 per cent. alcohol is  $1000 K = 1.4$  at  $85^\circ$ . The constant is considerably increased when sodium chloroacetate is substituted for the free acid, as indicated by the following numbers for  $1000 K$ . Sodium salt, 1.7 at  $65^\circ$ , 10.0 at  $80^\circ$ ; acid, 0.45 at  $65^\circ$ , 1.80 at  $80^\circ$ .

When sodium nitrate is used, the constant falls to about the same value as when water alone is used. The value  $1,000 K$  for the reaction between sodium hydroxide solution and sodium chloroacetate is 25.0 at  $80^\circ$  and 6.0 at  $65^\circ$ , and is increased by the presence of sodium chloride. The reaction between bromoacetic acid and silver nitrate, and also that between sodium bromoacetate and sodium hydroxide solution, take place more readily than in the case of the corresponding chloro-derivatives. The values for  $1000 K$  at  $65^\circ$  are bromoacetic acid and silver nitrate 42, sodium bromoacetate and sodium hydroxide 195, and at  $35^\circ$ , ethyl bromide and silver nitrate 85, and ethyl bromide and sodium hydroxide 6.5.

The conclusions that these reactions are preceded by ionisation and the reactions measured are the rates of ionisation are adversely criticised, and the view is expressed that the reaction is due to a complex of the type  $\text{Ag}^+\text{C}_2\text{H}_5\text{Br}$ .

J. J. S.

**Condition of Pseudo-acids in Aqueous Solution.** HEINRICH LEY and ARTHUR HANTZSCH (*Ber.*, 1906, 39, 3149—3160).—The authors show that pseudo-acids of the class of aliphatic nitro-compounds, like nitromethane, which have practically a neutral reaction in aqueous solution, do actually, however, undergo slight electrolytic dissociation in aqueous solution; the ionisation in water is never equal to nothing, as was formerly erroneously supposed by Hantzsch and his pupils. The dissociation constant of nitromethane, as deduced from its electrical conductivity in aqueous solution, is less than that of phenol. It is now concluded that there are no abnormal relationships between the affinity constant of nitromethane and the hydrolysis of its sodium salt.

Ethyl nitroacetate,  $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , is a pseudo-acid with a stronger tendency to ionisation than nitromethane. Its aqueous solution is distinctly acid, and it may be sharply titrated with sodium hydroxide and phenolphthalein. Determinations of its conductivity showed that it was about ten times as weak an acid as acetic acid. Solutions of its alkali salts have a distinctly alkaline reaction and are not neutral, as was formerly supposed.

Ethyl nitropropionate,  $\text{NO}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ , prepared by converting ethyl nitromalonate into ethyl nitroisosuccinate and then saponifying the latter, boils at  $80^\circ$  under 20 mm. pressure. Its sodium salt crystallises in needles and melts and decomposes at  $205^\circ$ . Determinations of the electrical conductivity of the acid showed that in strength it is of about the same order as carbonic acid. Its sodium salt has an alkaline reaction in aqueous solution, and here again there was no evidence of abnormal hydrolysis.

Dinitroethane, which is a stronger acid than the preceding nitro-



compounds, also forms an alkali salt which undergoes appreciable hydrolysis, the degree of which is greater than that of sodium acetate.  
A. McK.

**Stability of Aqueous and Alcoholic Solutions of Acetic Anhydride.** AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and HENRI BARBIER (*Bull. Soc. chim.*, 1906, [iii], 35, 625—629. Compare Abstr., 1905, i, 642).—Five and 10 per cent. solutions of the anhydride in cold water were made and set aside. From these solutions, equal aliquot parts were withdrawn every ten minutes and added to a slight known excess of aniline, which reacted quantitatively with the residual anhydride to form acetanilide. The acetic acid formed was then estimated by titration with normal sodium hydroxide solution in presence of phenolphthalein. The results are tabulated in the original, and show that the rate of hydration of the anhydride is fairly rapid at first and then decreases. It is also the more rapid the greater the initial dilution of the anhydride and the higher the temperature.

The alcoholic solutions contained (a) 10 per cent. of the anhydride or (b) alcohol and anhydride in molecular proportions, and equal aliquot portions were withdrawn at intervals of twenty-four hours and titrated with normal sodium hydroxide solution. It was observed that the amount of solution necessary to neutralise the acetic acid formed was less than the calculated quantity, unless considerable quantities of water were added before titration.

The results are tabulated in the original, and show that after a month esterification is incomplete, even in the solution initially containing anhydride and alcohol in molecular proportion. T. A. H.

**Preparation of the Anhydrides of Organic Acids.** RUDOLF SOMMER (D.R.-P. 171146).—The anhydrides of organic acids are readily prepared by heating their well-dried salts with silicon fluoride when the volatile anhydrides are distilled off from the mixture. The residue, when treated with sand and sulphuric acid, furnishes a fresh supply of silicon fluoride for the next operation. For example, silicon fluoride is passed into anhydrous sodium acetate at 200—220°, the gas is rapidly absorbed, and as this absorption ceases the acetic anhydride begins to distil over; the excess of silicon fluoride is collected in special condensing vessels. Potassium benzoate when similarly treated yields benzoic anhydride, which is extracted from the mixture with petroleum.  
G. T. M.

**Platinous Salts of Certain Organic Acids containing Sulphur.** LUDWIG RAMBERG (*Zeit. anorg. Chem.*, 1906, 50, 439—445).—*Platinous xanthate*,  $(\text{OEt} \cdot \text{CS} \cdot \text{S})_2\text{Pt}$ , obtained by interaction of potassium platinochloride and potassium xanthate in aqueous solution, occurs in flat, yellow prisms melting at 129—130°. It is insoluble in water, readily soluble in chloroform, and has the normal molecular weight in ethylene dibromide. It does not form additive compounds with hydrogen chloride or ammonia. *Platinous ethylthiolacetate*,  $(\text{SEt} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Pt}$ , obtained by interaction of potassium ethylthiol-

acetate and potassium platinochloride in aqueous solution, occurs in very light green crystals. It is very soluble in boiling water, partly polymerised in glacial acetic acid solution, and combines with 1 and 2 molecules of the halogen acids to form mono- and di-basic acids respectively. It also forms an additive compound with ammonia. *Platinous phenylthiolacetate*,  $(\text{SPh} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Pt}$ , obtained by interaction of sodium phenylthiolacetate and potassium platinochloride, occurs in very light green needles, melting with decomposition at  $225-226^\circ$ . It is slightly soluble in water, not polymerised in glacial acetic acid, forms acid additive compounds with the halogen acids, and with ammonia a compound  $(\text{SPh} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Pt} \cdot 4\text{NH}_3$ , which occurs in small colourless or yellow crystals. *Platinous hydrogen thiodiglycollate*,  $(\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Pt}$ , obtained by interaction of potassium platinochloride and potassium hydrogen thiodiglycollate or of platinous chloride and thiolacetic acid in hot concentrated aqueous solution, forms small, practically colourless needles. This compound is a dibasic acid; its acid potassium salt occurs in small, green needles.

It is pointed out that the xanthate differs entirely in its behaviour from the other compounds; this is due in all probability to the presence of two sulphur atoms, one of which is joined directly to platinum. The investigation of the other three salts and their additive compounds is being continued.

G. S.

**Constitution of Oleic Acid and the Action of Ozone on Fats.** ETTORE MOLINARI and E. SONCINI (*Ber.*, 1906, 39, 2735—2744. Compare Harries and Thieme, this vol., i, 227).—The iodine number 192 for the unsaturated acids obtained from pure linseed oil indicates the presence of acids containing triple linkings in addition to olefinic acids. The unsaturated acids readily combine with ozone, and the "ozone number," like the iodine number, is characteristic for each oil. The number is readily obtained by determining gravimetrically the amount of ozone absorbed by a solution of the oil in acetic acid or in a petroleum of high boiling point.

A simple method for the determination of the amount of ozone in a gaseous mixture is by absorption in olein and noting the increase in weight.

Oleic acid ozonide,  $\text{C}_{18}\text{H}_{34}\text{O}_5$ , is a colourless, transparent, viscous liquid, heavier than water. It does not absorb iodine and is stable up to a temperature of  $80-90^\circ$ . When subjected to dry distillation it yields a number of products which have not been completely investigated. When warmed with aqueous sodium hydroxide it yields a neutral product with a pleasant sharp odour and boiling at about  $190^\circ$ . In addition, four acids are produced, namely, *n*-nonylic acid, azealic acid,

an acid,  $\begin{array}{c} \text{O} \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H} \\ \text{O} \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H} \end{array}$ , which yields a soluble calcium salt and

*$\alpha$ -hydroxy- $\alpha$ -octyldecoic (hydroxydioctylacetic) acid*,  $\text{OH} \cdot \text{C}(\text{C}_8\text{H}_{17})_2 \cdot \text{CO}_2\text{H}$ , the calcium salt of which is insoluble in water. The last acid is a solid, waxy substance melting at about  $37^\circ$  and distilling at  $225^\circ$  under reduced pressure. The acid  $\text{C}_{18}\text{H}_{32}\text{O}_6$  is an oil which

decomposes when distilled under reduced pressure and may be oxidised quantitatively to azelaic acid.

The formation of these four acids is in complete harmony with the view that the double linking in the molecule of oleic acid is in the  $\theta$ -position (compare Saytzeff, *Abstr.*, 1893, i, 551; Baruch, *Abstr.*, 1894, i, 170; and Lewkowitsch, *J. Soc. Chem. Ind.*, 1897, 16, 391).

J. J. S.

**Oleic Acid Ozonide.** CARL D. HARRIES and CARL THIEME (*Ber.*, 1906, 39, 2844—2846. Compare this vol., i, 225; Molinari and Soncini, preceding abstract).—The ozonide obtained by the action of ozone on a chloroform solution of oleic acid has the composition  $C_{18}H_{34}O_6$  and is termed *oleic acid ozonide peroxide*. When purified by solution in ethyl acetate and precipitation with light petroleum, it forms a water-clear, vitreous product. When washed with water and sodium hydrogen carbonate solution, it yields the normal ozonide,  $C_{18}H_{34}O_5$ , which can also be prepared by the action of ozone on an acetic acid solution of oleic acid and subsequent precipitation with water and washing with the acid carbonate.

When boiled with water, the peroxide gives a much more intense hydrogen peroxide reaction than the normal ozonide. Both products yield with water, azelaic acid or its half aldehyde and nonylic acid or the corresponding aldehyde.

J. J. S.

**Lactonisation of  $\alpha\alpha$ -Dimethyl- $\beta\gamma$ -unsaturated Acids.** EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 580—588).—When  $\alpha\alpha$ -dimethylvinylacetic acid is dissolved in sulphuric acid and the solution is immediately poured into excess of water the principal product is  $\beta$ -hydroxy- $\alpha\alpha$ -dimethylbutyric acid, but if the solution be warmed trimethylethylene is formed. When dimethylvinylacetic acid is treated with hydrobromic acid, the bromine atom is added on, partly in the  $\beta$ - and partly in the  $\gamma$ -position, and the product on treatment with alkali carbonates yields a mixture of trimethylethylene and  $\alpha\alpha$ -dimethylbutyrolactone. With hydrogen iodide, the iodine atom takes the  $\beta$ -position and the product on treatment with alkali carbonates yields only trimethylethylene. The latter boils at 37—38°; its *dibromide* melts at 7° and boils at 57° under 14 mm. pressure.

*$\alpha\alpha$ -Dimethylbutyrolactone* is a liquid with a strong odour, melts at 6° and boils at 84° under 13 mm. pressure.  *$\alpha\alpha$ -Dimethylvalerolactone*, obtained by dehydrating dimethylpropenylacetic acid [mol. vol. (calc.) 138·9] with sulphuric acid, or by the action of alkali carbonates on  $\gamma$ -iodo- $\alpha\alpha$ -dimethylvaleric acid, prepared by adding hydrogen iodide to dimethylpropenylacetic acid, crystallises from light petroleum, melts at 52°, and has the mol. vol. 130·44 at 28° (compare Blanc, *Abstr.*, 1905, i, 680). When heated during twelve hours at 300° with an equal weight of potassium cyanide, the lactone yields potassium  $\gamma$ -cyano- $\alpha\alpha$ -dimethylvalerate, and this is converted by hydrochloric acid into *trimethylglutarimide*, which melts at 139° and sublimes readily.

Dimethylisopropenylacetic acid, when warmed with sulphuric acid,



yields first hydroxytrimethylbutyric acid and then tetramethylethylene (Reformatsky and Plesconossoff, *Abstr.*, 1896, i, 128).

*β-Bromo-ααβ-trimethylbutyric acid*,  $\text{CMe}_2\text{Br}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , obtained by the action of hydrobromic acid on dimethylisopropenylacetic acid, crystallises from a mixture of ether and light petroleum and decomposes at  $150^\circ$ . *β-Iodo-ααβ-trimethylbutyric acid*, obtained in an analogous manner, forms small crystals and decomposes at  $170^\circ$ . Both these halogen derivatives, when treated with alkali carbonates, yield tetramethylethylene. The latter boils at  $72^\circ$ . The *dibromide* separates from ether in characteristic quadratic prisms, and melts and decomposes at  $92^\circ$ .

Phenyldimethylvinylacetic acid is not readily attacked by hot sulphuric acid, and the sole product is *phenyltrimethylethylene*. This is a mobile liquid, boils at  $83^\circ$  under 12 mm. and at  $189^\circ$  under atmospheric pressure, yields oily products with bromine or hypochlorous acid, and on oxidation with permanganate furnishes acetone and acetophenone.

Sulphuric acid has no action on benzyldimethylvinylacetic acid. Hydroxyvinylpivalic acid, on treatment with sulphuric acid, furnishes a neutral product, which is not volatile under reduced pressure and may be a polymerised diethylenic hydrocarbon.

The foregoing results show that Fittig's rule for the diagnosis of  $\beta\gamma$ -unsaturated acids is not quite generally applicable. Acids of the type  $\text{CHR}\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$  readily yield lactones under these conditions, whilst acids of the type  $\text{CH}_2\cdot\text{CR}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$  furnish first the corresponding hydroxypivalic acids, and these are then decomposed into carbon dioxide and the unsaturated hydrocarbons. Acids of this class containing an aromatic nucleus are either unattacked by sulphuric acid, or yield a small quantity of the corresponding unsaturated hydrocarbon.

T. A. H.

**Abnormal Dehydration of Hydroxyalkylpivalic Esters. II.** EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 589—600. Compare *Abstr.*, 1905, i, 853, and this vol., i, 553).—When 'ethyl hydroxypivalate (ethyl  $\beta$ -hydroxy- $\alpha\alpha$ -dimethylpropionate) is dehydrated by means of phosphoric oxide, a mixture of ethyl tiglate and ethyl angelate is produced, the former preponderating. A portion of the ethyl tiglate is attacked by the phosphoric acid, yielding ethylene and tiglic acid, whilst the ethyl hydroxypivalate is also partially hydrolysed, and the acid liberated is decomposed, yielding hemipoly lactide.

Ethyl phenylhydroxypivalate (ethyl  $\beta$ -phenyl- $\alpha\alpha$ -dimethylhydracrylate), on treatment with phosphoric oxide, yields ethyl dimethylatropate (ethyl  $\alpha$ -phenyl- $\beta\beta$ -dimethylacrylate) as a principal product, with small quantities of ethyl isobutyrate, *phenyl dimethylethylene*,  $\text{CMe}_2\cdot\text{CHPh}$ , which boils at  $72^\circ$  under 15 mm. pressure, and yields an oily *dibromide*, and benzaldehyde (the semicarbazide of the latter melts at  $235^\circ$ ; compare Thiele and Stange, *Abstr.*, 1895, i, 251).

*Dimethylatropic acid*,  $\text{CMe}_2\cdot\text{CPh}\cdot\text{CO}_2\text{H}$ , separates from warm alcohol in brilliant needles and melts at  $151^\circ$ ; the *methyl* ester forms prismatic crystals, melts at  $32^\circ$ , and boils at  $142^\circ$  under 26 mm. pressure;

the *ethyl* ester is a mobile liquid and boils at  $136^{\circ}$  under 17 mm. pressure. When treated with bromine in carbon disulphide, the acid furnishes  $\alpha\beta$ -dibromo- $\alpha$ -phenyl- $\beta$ -methylbutyric acid, which crystallises from light petroleum in needles and melts at  $105^{\circ}$ . Ethyl dimethylatropate, on reduction with sodium, yields  $\alpha$ -phenyl- $\beta$ -methylbutyl alcohol,  $\text{CHMe}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{OH}$ , a viscous liquid with a thyme-like odour, and boiling at  $127^{\circ}$  under 15 mm. pressure; the *acetate* is a mobile, pleasant-smelling liquid, and boils at  $134^{\circ}$  under 15 mm. pressure. On oxidation with permanganate in presence of potassium hydrogen carbonate, dimethylatropic acid yields acetone and a mixture of benzoic and phenylglycollic acids.

*Ethyl dimethyltropate* is obtained, together with some ethyl- $\alpha\alpha$ -diphenylsuccinate, by condensing acetone with ethyl phenylbromoacetate in presence of zinc. It is a viscous liquid and boils at  $152^{\circ}$  under 19 mm. pressure. On hydrolysis with potassium hydroxide in alcohol, it furnishes no dimethyltropic acid, but only acetone and phenylacetic acid, and on treatment with phosphoric oxide yields ethyl dimethylatropate, identical with that obtained by the dehydration of ethyl phenylhydroxypivalate (see above).

When benzophenone is condensed with ethyl bromoisobutyrate, a very small quantity of *ethyl  $\beta$ -hydroxy- $\beta\beta$ -diphenylpivalate*,



is formed. This crystallises from light petroleum in superb needles and melts at  $101^{\circ}$ .

*Ethyl benzoylisobutyrate*,  $\text{CMe}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ , obtained by condensing benzonitrile with ethyl bromoisobutyrate in presence of zinc (Abstr., 1901, i, 252), is a slightly mobile liquid and boils at  $152^{\circ}$  under 20 mm. pressure. When condensed with bromobenzene in presence of zinc, no ethyl diphenylhydroxypivalate is formed.

*Benzophenone semicarbazone* crystallises from warm alcohol in small needles and melts at  $167^{\circ}$ .

T. A. H.

**A New Case of Tautomerism.** LUDWIG KNORR and WILLIAM HICKS (*Ber.*, 1906, 39, 3255—3257).—Ethyl thioacetoacetate (compare Buchka, Abstr., 1890, 28; Michaelis and Philipps, *ibid.*, 582) in alcoholic or benzene solution is converted rapidly into the enolic isomeride,  $\text{S}[\text{C}(\text{CO}_2\text{Et})\cdot\text{CMe}\cdot\text{OH}]_2$ , which is obtained best by keeping overnight an ethereal solution of the ester containing a trace of sodium hydroxide. It is a transparent oil which passes, slowly of itself, rapidly by shaking with sodium carbonate solution, into the solid ketonic modification.

C. S.

**Anhydrides of Dibasic Acids.** GERARDUS L. VOERMAN (*Bull. Soc. chim.*, 1906, [iii], 35, 665—666).—It is stated that Blaise and Houillon in a note recently published (*Bull. Soc. chim.*, 1906, [iii], 35, 199) have given the impression that the author's work (Abstr., 1904, i, 287; 1905, i, 13) on the molecular weights of the anhydrides of the dibasic acids showed that these substances were unimolecular, whereas it was shown that, although cryoscopic determinations in phenol gave normal results, ebullioscopic measurements in acetone gave results indicating that the anhydrides of the acids above adipic acid are polymerised.

T. A. H.

**Anhydrides of Dibasic Acids.** EDMOND E. BLAISE (*Bull. Soc. chim.*, 1906, [iii], 35, 666).—A reply to Voerman (see preceding abstract), in which a detailed consideration of the latter's results is promised in a forthcoming paper on the anhydrides of dibasic acids.

T. A. H.

**Decomposition of Malonic Ester Chloride.** HERMANN LEUCHS (*Ber.*, 1906, 39, 2641—2643).—The author has shown previously that when carbethoxyglycyl chloride is heated, it forms glycinecarboxylic anhydride with elimination of methyl chloride (this vol., i, 236). Ethyl malonate chloride has now been studied from the same standpoint.

When ethyl malonate chloride was heated for one hour at 125—130°, hydrogen chloride was evolved, but there was no evidence of the formation of ethyl chloride. The residue yielded the compound  $C_{13}H_{12}O_8$ , which separated from methyl alcohol in yellow prisms and melted at 170—180° (corr.). A determination of its molecular weight by the cryoscopic method in benzene solution gave a value corresponding with the formula quoted.

From methyl malonate chloride, the corresponding methyl compound,  $C_{11}H_8O_8$ , is formed in an analogous manner. It melts at 184—185° (corr.), and is similar in behaviour to the ethyl compound.

A. McK.

**Halogenated Aliphatic Acids. II.** WILHELM LOSSEN (*Annalen*, 1906, 348, 261—346. Compare Abstr., 1893, i, 142, and this vol., i, 59).—[With ERICH MENDTHAL.]—The velocity of the conversion of bromosuccinic acid into fumaric acid in the presence of water and at various concentrations (1—3 mol. proportions) has been investigated. The reaction is greatly accelerated by the presence of an alkali hydroxide, even when the solution remained acid after the addition of 1 mol. of the base. From a consideration of the possible configurations of the salts of bromosuccinic acid, it is concluded that the sodium hydrogen salt alone undergoes this decomposition.

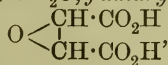
[With WALTHER BERGAU.]—Tribromosuccinic acid, prepared by a modification of Petri's method (Abstr., 1879, 373), crystallises in plates melting at 136° and is not hygroscopic; its *aniline* salt, prepared by mixing the ethereal or alcoholic solutions of its constituents, crystallises in prisms. An aqueous solution of the acid is decomposed quantitatively into dibromoacrylic acid, carbon dioxide, and hydrogen bromide. One hundred parts of a saturated solution of dibromoacrylic acid at 90° contains 8.2 parts of the acid.

When tribromosuccinic acid is treated with potassium hydroxide, it is converted quantitatively into dibromomaleic acid, provided that 3 mols. of the base are used for each mol. of the acid. On allowing gaseous ammonia to come in contact with a highly concentrated aqueous solution of tribromosuccinic acid, dibromomaleic acid is also produced, but if the acid is treated with strong aqueous ammonia, bromofumaric acid is formed. If a solution of tribromosuccinic acid in benzene is boiled, dibromomaleic acid is alone formed, a fact which



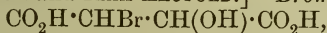
is not in agreement either with Wislicenus's experimental results or his theoretical views.

[With WALTHER SCHÖRK and MAX NIEHRENHEIM.]—*Chloromalic acid*,  $\text{CO}_2\text{H}\cdot\text{CHCl}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , is readily prepared from either sodium maleate or fumarate by adding chlorine water to the aqueous solution of the salt:  $\text{C}_4\text{H}_2\text{O}_4\text{Na}_2 + \text{Cl}_2 + \text{H}_2\text{O} = \text{C}_4\text{H}_4\text{O}_5\text{ClNa} + \text{NaCl}$ . The acid crystallises in monoclinic needles [ $a : b : c = 1.387 : 1 : 0.84904$ ;  $\beta = 65^\circ 41'$ ] melting at  $143^\circ$  and decomposing at a somewhat higher temperature. The *sodium* and *silver* salts are anhydrous, whilst the *barium* salt crystallises with  $3\text{H}_2\text{O}$ , and the *lead* salt with  $2\text{H}_2\text{O}$ . The *methyl* ester is an oily liquid. When subjected to dry distillation, chloromalic acid is mainly converted into chloromaleic acid, the same compound being also formed on heating the acid with a saturated solution of hydrochloric acid under pressure. On reduction with a zinc platinum couple in aqueous solution, malic acid is formed. When the aqueous solution is boiled, carbon dioxide, aldehyde, and hydrochloric and tartaric acids are produced, the rate of the decomposition increasing with the dilution:  $\text{C}_4\text{H}_5\text{O}_5\text{Cl} + \text{H}_2\text{O} = \text{C}_4\text{H}_6\text{O}_6 + \text{HCl}$ ;  $\text{C}_4\text{H}_5\text{O}_5\text{Cl} = \text{C}_2\text{H}_4\text{O} + \text{CO}_2 + \text{HCl}$ . A similar decomposition occurs when potassium hydrogen chloromaleate is boiled in aqueous solution. The normal salt decomposes in a similar manner, but the main reaction is the formation of aldehyde and carbon dioxide. When boiled with an excess (3 mols.) of *N*-potassium hydroxide, a reaction takes place quantitatively according to the following equation:  $\text{C}_4\text{H}_5\text{O}_5\text{Cl} + 3\text{KOH} = \text{C}_4\text{H}_4\text{O}_6\text{K}_2 + \text{KCl} + 3\text{H}_2\text{O}$ , *fumarylglglycidic acid*,



being produced.

[With HANS DUECK and MAX LEOPOLD.]—*Bromomalic acid*,



is prepared by the action of bromine water on an alkaline solution of fumaric acid; the acid forms monoclinic crystals, isomorphous with chloromalic acid and melting at  $132\text{--}134^\circ$ . The *sodium* salt is anhydrous and decomposes at  $100^\circ$ ; the *barium* salt crystallises with 3 and  $4\text{H}_2\text{O}$ , whilst the *lead* and *silver* salts are anhydrous. When subjected to dry distillation, carbon dioxide, hydrogen bromide, and bromomaleic acid are formed. If the aqueous solution is boiled, carbon dioxide, aldehyde, and hydrobromic and racemic acids are produced, whilst, as in the case of chloromalic acid, the action of sodium hydroxide leads quantitatively to the formation of fumarylglglycidic acid. When an attempt was made to prepare this acid from barium maleate, a bromomalic acid was obtained, which crystallised with  $\text{H}_2\text{O}$  and melted at  $63\text{--}65^\circ$ ; its salts are identical with those of the anhydrous acid, and on melting it yields the crystals of the latter. If a solution of molecular proportions of the anhydrous acid and water are made in ether or chloroform, the anhydrous acid crystallises out on evaporation, but if the solution is sown with a crystal of the hydrated acid, the latter separates. The decomposition of the hydrated acid in water is similar to that of the anhydrous, but it was found that mesotartaric acid was formed at the same time as racemic acid. The barium salts of both acids behaved in a similar manner when their solutions were

boiled. Both acids were converted into fumarylglcydic acid with equal ease.

[With WALTHER SCHÖRK, MAX NIEHRENHEIM, HANS DUECK, and MAX LEOPOLD].—Fumarylglcydic acid, prepared either from chloro- or bromo-malic acid, forms prismatic crystals melting at  $203^{\circ}$ ; its sodium salt,  $C_4H_3O_5Na \cdot H_2O$ , crystallises in plates, the calcium, barium, and the lead salts each crystallise with  $2H_2O$ , whilst the silver salt is anhydrous and explosive. The methyl ester,  $O < \begin{matrix} CH \cdot CO_2Me \\ | \\ CH \cdot CO_2Me \end{matrix}$ , prepared from the silver

salt and methyl iodide, crystallises in needles melting at  $73^{\circ}$ , and reacts neither with acetyl chloride nor with phenylcarbimide; hence no hydroxyl group is present. The acid chloride, prepared from the acid and phosphorus pentachloride, forms scaly crystals melting at  $53^{\circ}$  and boiling at  $90-93^{\circ}$  under 40 mm. pressure. The diphenyl ester,  $C_2H_2O(CO_2Ph)_2$ , prepared from the acid chloride and phenol, forms crystals melting at  $133^{\circ}$ . The amide,  $C_2H_2O(CO \cdot NH_2)_2$ , prepared from the methyl ester and alcoholic ammonia, is a microcrystalline solid melting and decomposing at  $225^{\circ}$ .

On boiling the fumarylglcydic acid with water, carbon dioxide, aldehyde, and racemic and mesotartaric acids are formed. Concentrated hydrochloric and hydrobromic acids convert the acid into the corresponding halogen malic acids; with ammonia, it combines to form aminomalic acid.

[With ERICH MENDTHAL].—When aqueous solutions of bromofumaric or bromomaleic acids are boiled, they are decomposed into carbon dioxide, aldehyde, and propargylic acid. A similar decomposition occurs if the normal sodium or sodium hydrogen salts are heated in aqueous solution, but in the presence of excess of alkali hydroxide, on the other hand, acetylenedicarboxylic acid is the main product, a portion afterwards decomposing into propargylic acid. Under all conditions, bromofumaric acid decomposes more rapidly than bromomaleic acid; the normal salts decompose most readily, whilst the free acids and the hydrogen salts are relatively stable.

On reducing either of the acids with sodium amalgam or with zinc, fumaric and succinic acids are produced.

[With ADOLF TREIBICH].—Anhydrous acetylenedicarboxylic acid is prepared by treating the ethereal solution of the hydrated acid with calcium chloride. When a concentrated aqueous solution of the acid is treated with the calculated quantity of bromine vapour, it is converted quantitatively into dibromofumaric acid together with a small quantity of dibromomaleic acid. Acetylenedicarboxylic acid is easily oxidised by permanganate to oxalic acid and carbon dioxide.

The action of bromine on a dilute aqueous solution of acetylenedicarboxylic acid is very complicated, and is represented by the following equations:  $C_4H_2O_4 + 4H_2O + 5Br_2 = 4CO_2 + 10HBr$ ;  $C_4H_2O_4 + 4H_2O + 3Br_2 = 2C_2H_2O_4 + 6HBr$ ;  $C_4H_2O_4 + HBr = C_4H_3O_4Br$ ;  $C_4H_2O_4 + Br_2 = C_4H_2O_4Br_2$ .

[With WALTHER BERGAU].—The action of chlorine on acetylenedicarboxylic acid and of chlorine or bromine on sodium acetylenedicarboxylate was investigated under various conditions, but in no case was a simple reaction observed.

K. J. P. O.

**Preparation of Peroxide Acids from the Anhydrides of Dibasic Acids.** FREDERICK STEAINS & Co. (D.R.-P. 170727).—Peroxide acids having pronounced antiseptic and germicidal properties are produced on shaking the anhydrides of the dibasic acids with a dilute aqueous solution of hydrogen peroxide until a precipitate is produced. Peroxide-phthalic acid, a substance already described, can be prepared in this way, and the reaction takes place equally readily with succinic and glutaric anhydrides.

*Peroxide succinic acid*,  $O_2(CO \cdot CH_2 \cdot CH_2 \cdot CO_2H)_2$ , separates in colourless tabular crystals slightly soluble in water, alcohol, ethyl acetate, acetic acid, or ether, and insoluble in chloroform or benzene. Water slowly hydrolyses it, yielding molecular proportions of succinic acid and succinic peracid,  $CO_2H \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot OH$ .

*Peroxide glutaric acid*,  $O_2(CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H)_2$ , is prepared similarly by shaking glutaric anhydride for half an hour with 7·8 per cent. aqueous hydrogen peroxide at 30°.

G. T. M.

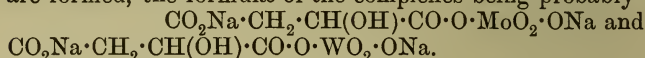
**Solubility of Alkaline Earth Malates in Water.** H. CANTONI and M. BASADONNA (*Bull. Soc. chim.*, 1906, [iii], 35, 727—737. Compare Abstr., 1904, i, 142).—Strontium malate is the most soluble of the three salts and its solubility increases greatly with rise of temperature. The least soluble salt is calcium malate, and its solubility diminishes as the temperature is increased. The solubility of barium malate is intermediate between that of the calcium and strontium salts and increases very slightly with rise of temperature. The experimental results are tabulated in detail in the original, which also gives a number of solubility curves for the three salts, and details of the methods employed in conducting the experiments and in estimating malic acid.

T. A. H.

**Increase and Reversal of Rotation. I. Complex Molybdyl and Tungstyl Malates.** HERMANN GROSSMANN and HEINZ PÖTTER (*Zeit. physikal. Chem.*, 1906, 56, 577—604. Compare this vol., ii, 211; also Itzig, Abstr., 1901, i, 580).—The rotatory power of solutions containing malic acid and ammonium molybdate, sodium molybdate, or sodium tungstate varies often in a peculiar manner when the concentration and the temperature are altered. The authors have made an extensive study of these variations, their measurements covering the following molecular combinations: (1) 1 mol.  $C_4H_6O_5$  + 0·5 mol.  $(NH_4)_2MoO_4$  (compare Grossmann and Pötter, Abstr., 1904, ii, 153); (2) 1 mol.  $C_4H_6O_5$  + 0·5 mol.  $Na_2MoO_4$ ; (3) 1 mol.  $C_4H_6O_5$  + 1 mol.  $Na_2MoO_4$ ; (4) 1 mol.  $C_4H_6O_5$  + 1·5 mols.  $Na_2MoO_4$ ; (5) 1 mol.  $C_4H_6O_5$  + 2 mols.  $Na_2MoO_4$ ; (6) 1 mol.  $C_4H_6O_5$  + 4 mols.  $Na_2MoO_4$ ; (7) 1 mol.  $C_4H_6O_5$  + 1 mol.  $Na_2MoO_4$  + 1 mol.  $MoO_3$ ; (8) 1 mol.  $C_4H_6O_5$  + 0·5 mol.  $Na_2WO_4$ ; (9) 1 mol.  $C_4H_6O_5$  + 1 mol.  $Na_2WO_4$ ; (10) 1 mol.  $C_4H_6O_5$  + 1·5 mols.  $Na_2WO_4$ ; (11) 1 mol.  $C_4H_6O_5$  + 2 mols.  $Na_2WO_4$ . The observations indicate that the peculiar variations of rotation are in some cases due to the formation of molybdyl and tungstyl dimalates, which are highly active complexes and are but slightly affected by changes of concentra-



tion and temperature. In other cases molybdbl and tungstyl malates are formed, the formulæ of the complexes being probably



The rotation of the molybdbl malate is at the ordinary temperature but little affected by change of concentration, but with rise of temperature it decreases regularly and markedly at all concentrations. In the case of the tungstyl malate, dilution and rise of temperature both produce a marked increase in rotation. When 1 molecule of malic acid is mixed with more than 1 molecule of sodium molybdate or tungstate, complexes are formed, which are sometimes dextrorotatory, sometimes levorotatory, and which are very sensitive to changes of concentration and temperature. The molybdbl complexes of this kind appear to be completely resolved at high dilution into the 1 : 1 salt and inactive sodium molybdate: this splitting up of the higher complex is not quite so definite in the case of the tungstyl compounds. That so many cases of maxima, minima, and reversal of rotation have been observed by the authors is probably due to the formation in the concentrated solutions of slightly stable additive products, characterised by rotations of opposite sign.

J. C. P.

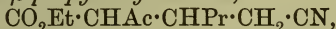
**Preparation of Mercury Cholates.** J. D. RIEDEL (D.R.-P. 171485).—Mercury cholates are not easily obtained by the double decomposition between cholic acid and the inorganic mercury salts, for in these cases the product is either colloidal or contains excess of the corresponding mercury oxide. Either mercurous or mercuric cholate may, however, be produced readily by employing the mercury salt of an organic acid such as acetic acid. A 5 to 10 per cent. aqueous solution of a soluble cholate is introduced, with vigorous stirring, into a solution of mercurous or mercuric acetate, when the corresponding mercury salt is deposited as a yellowish-white precipitate which can be readily collected and dried.

*Mercurous cholate*,  $\text{C}_{24}\text{H}_{39}\text{O}_5\text{Hg}$ , is a yellowish-white, insoluble powder, decomposed by alkalis or alcohol. *Mercuric cholate*,  $(\text{C}_{24}\text{H}_{39}\text{O}_5)_2\text{Hg}$ , is similar in appearance, but rather more soluble, particularly in acidified water or in aqueous solutions of sodium or potassium chloride; it is also decomposed by alcohol.

G. T. M.

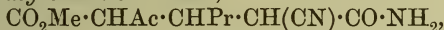
**New Derivatives of  $\delta$ -Ketonic Acids.** ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1906, 41, 842—861. Compare Abstr., 1898, i, 274; 1900, i, 52, 111; 1901, i, 341, 630; 1902, i, 819; 1903, i, 736; 1905, i, 821).—The interaction of molecular proportions of ethyl acetoacetate, ethyl cyanoacetate, and *n*-butaldehyde in presence of ammonia yields the ammonium derivative of propyldicyanodioxypyridine (Abstr., 1902, i, 819) and  $\gamma$ -carbethoxy- $\gamma$ -acetyl- $\beta$ -propylbutyronitrile- $\alpha$ -amide,  $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CHPr}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$ , which crystallises from water in shining, colourless prisms, melts at 205—206°, and dissolves in alcohol or acetic acid. It has a neutral reaction, does not absorb bromine and is soluble in sodium hydroxide solution with evolution of ammonia. When heated with excess of

barium hydroxide solution, it yields 2 mols. of ammonia and  $\gamma$ -carbethoxy- $\gamma$ -acetyl- $\beta$ -propylbutyric acid (?), which forms a soluble barium salt. On heating with hydrochloric acid of sp. gr. 1.19, it yields  $\gamma$ -carbethoxy- $\gamma$ -acetyl- $\beta$ -propylbutyronitrile,



which crystallises from water in long, colourless needles, or from alcohol in prisms, melts at  $125-126^\circ$ , has a neutral reaction, and reduces permanganate. When heated with 60 per cent. sulphuric acid, it gives  $\gamma$ -carbethoxy- $\gamma$ -acetyl- $\beta$ -propylbutyric acid (?).

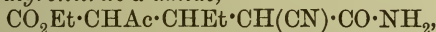
If the ethyl acetoacetate employed in the above reaction is replaced by the corresponding methyl ester, there is obtained  $\gamma$ -carbmethoxy- $\gamma$ -acetyl- $\beta$ -propylbutyronitrile- $\alpha$ -amide,



which separates from water in crystals melting at  $248-249^\circ$ .

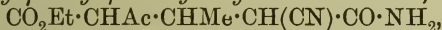
When mixed in molecular proportions, propaldehyde, ethyl acetoacetate, and ethyl cyanoacetate in presence of ammonia yield (1) the ammonium derivative of dicyanodioxymethylpyridine, (2) a compound

which is probably  $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{CO}_2\text{Et}) \\ \text{CO} - \text{C}(\text{CN}) \end{smallmatrix} \text{CEt}$ , and (3)  $\gamma$ -carbethoxy- $\gamma$ -acetyl- $\beta$ -ethylbutyronitrile- $\alpha$ -amide,



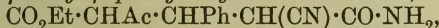
which separates from water in crystals melting at  $199-200^\circ$ , and, on boiling with hydrochloric acid, yields  $\gamma$ -carbethoxy- $\gamma$ -acetyl- $\beta$ -ethylbutyronitrile (?),  $\text{CO}_2\text{Et} \cdot \text{CHAc} \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{CN}$ , crystallising from water in long needles melting at  $92-94^\circ$ , and dissolving in ether or alcohol.

Acetaldehyde, ethyl acetoacetate, ethyl cyanoacetate and ammonia yield methyl dicyanoglutaconimide, ethyl hydrocollidinedicarboxylate, and  $\gamma$ -carbethoxy- $\gamma$ -acetyl- $\beta$ -methylbutyronitrile- $\alpha$ -amide,



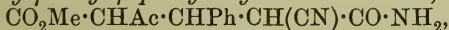
which melts at  $212-213^\circ$  and is soluble in alcohol or water.

$\gamma$ -Carbmethoxy- $\gamma$ -acetyl- $\beta$ -phenylbutyronitrile- $\alpha$ -amide,



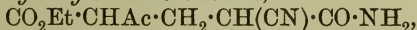
obtained with other products by the interaction of benzaldehyde, ethyl acetoacetate, methyl or ethyl cyanoacetate, and ammonia, crystallises from alcohol in shining, acicular prisms melting at  $225-226^\circ$  and exhibits characters resembling those of the corresponding compounds prepared from aliphatic aldehydes. When heated with hydrochloric acid of sp. gr. 1.19 in presence of alcohol, it yields  $\gamma$ -carbethoxy- $\gamma$ -acetyl- $\beta$ -phenylbutyronitrile, which melts at  $152-154^\circ$  and is soluble in ether.

$\gamma$ -Carbmethoxy- $\gamma$ -acetyl- $\beta$ -phenylbutyronitrile- $\alpha$ -amide,



forms heavy, colourless crystals melting at  $234-235^\circ$  and dissolves in water or alcohol.

The interaction of formaldehyde, ethyl acetoacetate, and ethyl cyanoacetate in presence of ammonia yields only a small proportion of  $\gamma$ -carbethoxy- $\gamma$ -acetylbutyronitrile- $\alpha$ -amide,



which crystallises in short, heavy prisms melting at  $178-180^\circ$ , the main product being a dicyano-pyridine derivative.

T. H. P.

**Synthetical Experiments with *d*-Gluconic Acid. II.** CARL PAAL and FRANZ HÖRNSTEIN (*Ber.*, 1906, 39, 2823—2827. Compare this vol., i, 400).—The lactone of tetra-acetyl-*d*-gluconic acid is obtained as a transparent, faintly yellow-coloured, gummy mass, giving correct results on analysis if care be taken to avoid the use of alcohol in isolating it. It is sparingly soluble in hot water and in benzene solution has  $[\alpha]_D + 70.86^\circ$  at  $21^\circ$ . The experimental methods have been improved so as to prepare 1 : 1-diphenyl-*d*-sorbitol in a crystalline form melting at  $157\text{--}160^\circ$ ; the cold supersaturated solutions in water and alcohol have  $[\alpha]_D + 71.25^\circ$  and  $+74.75^\circ$  respectively at  $25^\circ$ .

E. F. A.

**Synthetical Experiments with *d*-Galactonic Acid.** CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1906, 39, 2827—2833. See preceding abstract).—*Tetra-acetyl-d-galactonic lactone*, prepared by heating the lactone with acetic anhydride, is obtained as a transparent, tough gum having  $[\alpha]_D - 1.04^\circ$  at  $20^\circ$ ; the product obtained by acetylating at  $50\text{--}60^\circ$  has  $[\alpha]_D - 8.5^\circ$  at  $20^\circ$ . 1 : 1-Diphenyl-*d*-galactohexitol, obtained by heating the acetyl-lactone, dissolved in benzene, with magnesium phenyl bromide crystallises in ball-like aggregates of colourless, faintly-glistening needles melting at  $157\text{--}160^\circ$  and containing  $\text{H}_2\text{O}$ . It is less soluble in water and more so in alcohol than diphenylsorbitol. The supersaturated solution in water has  $[\alpha]_D + 72.9^\circ$  at  $20^\circ$ , and in alcohol  $[\alpha]_D + 56.23^\circ$  at  $20^\circ$ . A by-product of the action of magnesium phenyl bromide is described melting at  $93\text{--}97^\circ$  and yielding, when heated with potassium hydroxide, crystals melting at  $98\text{--}100^\circ$  which show  $[\alpha]_D - 106.4^\circ$  at  $20^\circ$ .

E. F. A.

**Physiological Relationships of the Proteids containing Sulphur. IV.** ERNST FRIEDMANN and JULIUS BAER (*Beitr. chem. Physiol. Path.*, 1906, 8, 326—331. Compare Abstr., 1902, i, 731; 1903, i, 75, 301; 1904, i, 165).—A specimen of pure proteid cystein or  $\alpha$ -amino- $\beta$ -thiolactic acid disulphide, when heated in the form of its hydrochloride with water at  $145^\circ$  for 1.5 hours and then reduced with tin and hydrochloric acid, yields  $\alpha$ -thiolactic acid. The formation of this acid is not due, as suggested by Mörner (*Abstr.*, 1904, i, 836), to the presence of an isomeric cystein in the natural product, but is formed from the pure disulphide of  $\alpha$ -amino- $\beta$ -thiolactic acid, probably through the intermediate formation of pyruvic acid, as this is known to yield a product with hydrogen sulphide which on reduction gives  $\alpha$ -thiolactic acid.

J. J. S.

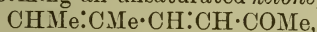
**Zinc Formaldehydesulphoxylate.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172217).—Sodium formaldehydesulphoxylate was formerly isolated by the fractional crystallisation from the other substances produced by the interaction of formaldehyde and sodium hyposulphite. It is now found that formaldehydesulphoxylic acid forms a sparingly soluble zinc salt which is readily separated from the sulphide present. The separation is best effected by treating a solution of zinc formaldehydehyposulphite with sodium carbonate in accordance with the following equation:  $2\text{ZnS}_2\text{O}_4, 2\text{CH}_2$



+  $\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} = 2\text{ZnSO}_3 \cdot \text{CH}_2\text{O} \cdot \text{H}_2\text{O} + 2\text{NaHSO}_3 \cdot \text{CH}_2\text{O} + \text{CO}_2$ . A solution of zinc hyposulphite,  $\text{ZnS}_2\text{O}_4$  (100 grams) is treated with formaldehyde until it loses its power of reducing indigotinsulphonic acid in the cold, and then 25 grams of dry sodium carbonate are added. The new zinc salt, which separates slowly, is washed and dried; it is a crystalline substance which is stable in the air and which, on digestion with aqueous sodium carbonate, yields a solution of sodium formaldehydesulphoxylate.

G. T. M.

**Condensation of Tiglic Aldehyde with Acetone.** FRITZ DAUTWITZ (*Monatsh.*, 1906, 27, 773—776).—Tiglic aldehyde, prepared by heating a mixture of acetaldehyde and propaldehyde with sodium acetate solution, condenses with acetone in aqueous sodium hydroxide solution at 5—10°, forming an unsaturated ketone,



which is obtained as a colourless, strongly refracting, mobile oil. It has a characteristic aromatic odour, boils at 92—93° under 12 mm. pressure, is rapidly oxidised by air forming a resin, and forms an additive compound with 2 mols. of bromine. The oxime,  $\text{C}_{18}\text{H}_{19}\text{ON}$ , crystallises from light petroleum and melts at 71°, forming a viscous, colourless, strongly refracting oil, which boils at 140—141° under 13 mm. pressure.

G. Y.

**Oxidation of Acyloins of the Fatty Series: some  $\alpha$ -Diketones and their Derivatives.** LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 650—654. Compare Abstr., 1905, i, 573, and this vol., i, 782, 783, 784).—The authors confirm Ponzio's observation (Abstr., 1901, i, 452) that acyloins are not readily converted into  $\alpha$ -diketones by the usual oxidising agents. They find, however, that yields of 50 per cent. and upwards of the diketones can be obtained by the application of Sabatier and Senderens' catalytic process (Abstr., 1903, i, 454, and 1905, i, 254) to the acyloins. The authors now find that the statement formerly made (Locquin, Abstr., 1905, i, 20), that the higher  $\alpha$ -diketones which do not contain the  $\text{H}_3\text{C}\cdot\text{CO}$  group do not form sodium hydrogen sulphite compounds, is inaccurate; the compounds are, however, unstable and difficult to isolate in the e cases.

*Diisobutyl* has a sp. gr. 0.912 at 4°/0° and boils at 144—145°. The *nonoxime* boils at 135° under 10 mm. pressure, and the *dioxime* crystallises from boiling benzene and melts at 171.5°. When *diisobutyl* is treated with magnesium methyl iodide, a *product* is obtained, which boils at 75—80° under 11 mm. pressure, and may have the constitution  $\text{COPr}^\beta \cdot \text{CMePr}^\beta \cdot \text{OH}$ . With magnesium phenyl bromide, a liquid is produced, which boils at 137° under 11 mm. pressure and may consist of the substance  $\text{COPr}^\beta \cdot \text{CPhPr}^\beta \cdot \text{OH}$ , with a trace of its dehydration product,  $\text{COPr}^\beta \cdot \text{CPh}:\text{CMe}_2$ .

T. A. H.

**Influence of some Mineral Matters on the Liquefaction of starch.** JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1906, 43, 363—365).—It was previously shown (*ibid.*, May 15, 1906) that the lime present in starch has considerable influence on the viscosity. Experiments with starch, previously washed until nearly

free from calcium and magnesium, showed that ammonia, sodium carbonate, magnesium carbonate, and calcium carbonate have about the same effect, whilst alumina is without action.

When starch containing the usual bases is treated with sulphuric or phosphoric acid until about neutral (methyl-orange), it very readily loses its viscosity when heated under pressure. N. H. J. M.

**Mechanism of the Influence of Acids, Bases, and Salts in the Liquefaction of Starch Paste.** AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1906, 143, 380—383. Compare Abstr., 1904, i, 211, 374; 1905, i, 164, 574, 624; preceding abstract). When starch paste is made neutral to methyl-orange by the addition of sulphuric acid and then heated at 120°, its viscosity is very greatly diminished, but if disodium hydrogen phosphate is added to the neutralised paste before heating, the viscosity is increased, and becomes equal to that of the original paste when the quantity of the salt added is two and a half times that of the equivalent of the acid. The addition of neutral salts, such as magnesium or calcium sulphate or of sodium dihydrogen phosphate, to the neutralised starch paste effects no change in its viscosity, nor is the viscosity of the original paste changed by the addition of disodium hydrogen phosphate or of sodium dihydrogen phosphate. The effect of sodium hydroxide in retarding the liquefaction of neutralised starch paste is much more marked than that of disodium hydrogen phosphate. It follows, therefore, that the liquefaction of neutralised starch paste is partly due to the transformation of the secondary phosphates present in the starch into primary phosphates, that it is not affected by the addition of salts neutral to methyl-orange, but is retarded by the addition of salts alkaline to this reagent, and checked altogether by traces of free alkali.

M. A. W.

**Starchy Substances studied by the aid of our knowledge of the Colloidal State.** G. MALFITANO (*Compt. rend.*, 1906, 143, 400—403).—A theoretical paper. Fernbach has shown that starch contains 0.2 per cent. of phosphorus in the form of phosphates even after maceration with hydrochloric acid (Abstr., 1904, i, 294); the author therefore regards a clear starch solution as a colloidal solution in which the granules are formed of starch molecules grouped round the  $\text{:PO}_4$  ion,  $[(\text{C}_6\text{H}_{10}\text{O}_5)_n\text{PO}_4]_i$ , the composition varying with the nature of the free electrolytes in the liquid medium, and subject to the laws already established in the case of a colloidal solution of ferric hydroxychloride (compare Abstr., 1905, ii, 459; this vol., ii, 33, 450, 526).

M. A. W.

**Action of Acyl Chlorides on Mixtures of Amines.** FRANK DAINS (*J. Amer. Chem. Soc.*, 1906, 28, 1183—1188).—This investigation was carried out with the object of ascertaining whether, when a mixture of two amines in molecular proportions is treated with an acyl chloride, any preference is shown as to the amine attacked, and also determining the conditions which govern any such preference. The results show that when there is any appreciable difference of basic

between the two amines, the acyl derivative of the more negative is largely or exclusively produced together with the salt of the more positive amine. E. G.

**Compounds of Chromium Tetroxide with Ethylenediamine and Hexamethylenetetramine.** KARL A. HOFMANN (*Ber.*, 1906, 39, 3181—3184).—*Ethylenediamine chromate*,  $\text{H}_2\text{CrO}_4 \cdot \text{C}_2\text{H}_8\text{N}_2$ , prepared by the addition of ethylenediamine hydrate to an aqueous solution of chromic acid, forms orange-coloured, tetragonal plates, and is sparingly soluble in water.

The compound  $\text{CrO}_4 \cdot \text{C}_2\text{H}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$ , prepared by cooling in ice the filtrate obtained from a mixture of chromic acid, water, and ethylenediamine hydrate and then adding hydrogen peroxide, forms a glistening, greyish-green, crystalline powder, which deflagrates on heating.

The compound  $\text{CrO}_4 \cdot \text{C}_6\text{H}_{12}\text{N}_4$ , prepared in a similar manner from hexamethylenetetramine, separates in "reddish-brownish-yellow" hexagonal crystals. When heated it deflagrates. A. McK.

**Ethylene- and Propylene-diamine Compounds of Palladium.** ALEXANDER GUTBIER and M. WOERNLE (*Ber.*, 1906, 39, 2716—2720. Compare Abstr., 1905, i, 584, 876; ii, 534; this vol., i, 244, 402).—When an aqueous solution of ethylenediamine or propylenediamine is added to one of a palladous haloid, rose- or flesh-coloured precipitates are obtained, having the composition  $\text{PdD}_2\text{X}_2, \text{PdX}_2$  (where D is the diamine and X is chlorine or bromine). They are soluble in excess of the base, and from the yellow solutions dilute halogen acids precipitate yellow needles of the palladosammines.

*Palladous ethylenediamine chloride*,  $\text{PdDCl}_2$ , *bromide*,  $\text{PdDBr}_2$ , *iodide*,  $\text{PdDI}_2$ , and the corresponding propylenediamine compounds, dissolve in concentrated halogen acids, forming dark-coloured solutions, from which, on cooling, substances of the preceding type separate. Substances of the type  $\text{PdX}_2 \cdot \text{D}_2\text{HX}$  have been prepared, and are capable of combining with two atoms of halogen to form compounds of the type  $\text{PdX}_4 \cdot \text{D}_2\text{HCl}$ . C. S.

**Synthesis of Hydroxy- and Diamino-acids. III.  $\alpha\alpha$ -Diaminoazelaic Acid,  $\alpha\beta$ -Diaminobutyric Acid, and  $\beta$ -Amino- $\alpha$ -hydroxybutyric Acid.** CARL NEUBERG and MAX FEDERER (*Chem. Centr.*, 1906, ii, 764—766; from *Biochem. Zeit.*, 1, 282—298. Compare Abstr., 1905, i, 687).—When treated with bromine in presence of phosphorus, azelaic acid yields  $\alpha\alpha$ -dibromoazelaic acid in the form of a yellow, non-crystallisable oil. When heated with concentrated ammonia and ammonium carbonate at 120—125°, this yields  $\alpha\alpha$ -diaminoazelaic acid in the form of microscopic crystals, which dissolve in hot water and are readily soluble in alkali hydroxides or mineral acids. It forms insoluble copper, silver, mercury, and lead salts, and combines with phenylcarbimide to form a crystalline phenylhydantoic acid, which melts at about 120°; the diethyl ester is an oil.

$\alpha\beta$ -Diaminobutyric acid was obtained from  $\alpha\beta$ -dibromobutyric acid in a similar manner in 24 per cent. yield. With phenylcarbimide, it yields a crystalline compound,  $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_4$ , melting at 238°. With



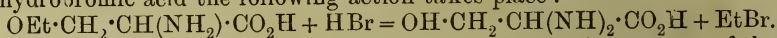
picric acid it yields a picrate,  $C_{10}H_{13}O_9N_5 \cdot 2H_2O$ , which is hygroscopic and decomposes at about  $90^\circ$ .

When the product obtained by the action of concentrated ammonia is kept for some time, it deposits rhombic crystals of  $\beta$ -amino- $\alpha$ -hydroxybutyric acid. Iminobutyric acid is probably formed as an intermediate product, and this then combines with water. It yields a copper salt,  $NH_2 \cdot CHMe \cdot CH \begin{smallmatrix} \text{CO-} \\ \text{O-Cu} \end{smallmatrix} O$ , and with  $\alpha$ -naphthylcarbimide it gives the crystalline  $\alpha$ -naphthylhydantoic acid, which decomposes at about  $170^\circ$ .

H. M. D.

**A New Synthesis of Serine.** HERMANN LEUCHS and WALTER GEIGER (*Ber.*, 1906, 39, 2644—2649).—The authors describe a third method of synthesising serine, the acid having been formerly synthesised by Erlenmeyer, jun. (*Abstr.*, 1903, i, 29) and by E. Fischer and Leuchs (*Abstr.*, 1903, i, 12).

When chloroacetal,  $CH_2Cl \cdot CH(OEt)_2$ , is heated with sodium ethoxide it forms ethoxyacetal,  $OEt \cdot CH_2 \cdot CH(OEt)_2$ , which, when boiled with dilute sulphuric acid, is converted into ethoxyacetaldehyde,  $OEt \cdot CH_2 \cdot CHO$ . The isolation of this product from the reaction mixture was not necessary, since the latter may be submitted directly to the cyanohydrin reaction by consecutive treatment with ammonia, hydrogen cyanide, and hydrochloric acid, when  $\beta$ -ethoxy- $\alpha$ -alanine,  $OEt \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$ , is formed. The latter compound need not be isolated, since when the reaction mixture is boiled with concentrated hydrobromic acid the following action takes place:



The yield of serine obtained in this manner is 35—40 per cent. of the theoretical, calculated on the ethoxyacetal used.

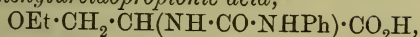
Various derivatives of  $\beta$ -ethoxy- $\alpha$ -alanine, serine, and ethoxyacetaldehyde are described.

$\gamma$ -Phenyl- $\alpha$ -hydroxymethylhydantoin,  $C_{10}H_{10}O_3N_2$ , prepared by evaporating to dryness a mixture of the alkaline solution of  $\beta$ -hydroxy- $\alpha$ -phenylureidopropionic acid and hydrochloric acid, separates from water in needles and melts at  $168$ — $169^\circ$  (corr.).

Ethyl carboxymethylserine,  $CO_2Me \cdot NH \cdot CH(CH_2 \cdot OH) \cdot CO_2Et$ , was prepared as follows: a current of dry hydrogen chloride was passed through an ethyl-alcoholic solution of serine until the latter had dissolved and the mixture then heated for one hour at  $100^\circ$ . The free ethyl serine was then liberated from the resulting hydrochloride and treated with a mixture of methyl chlorocarbonate and sodium carbonate. Ethyl carboxymethylserine is a viscid oil, which boils at  $181$ — $182^\circ$  under 12 mm. pressure.

$\beta$ -Ethoxy- $\alpha$ -alanine,  $OEt \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$ , may be obtained as an intermediate product in the synthesis of serine just described and melts and decomposes at  $256^\circ$  (corr.). Its aqueous solution has a sweet taste, reacts faintly acid towards litmus, and assumes a deep blue tint when boiled with copper oxide. It is sparingly soluble in water and separates from 90 per cent. alcohol in needles. Its copper salt is described. When heated with concentrated hydrochloric acid, it is converted into serine.

$\beta$ -Ethoxy- $\alpha$ -phenylureidopropionic acid,



prepared by the addition of phenylcarbimide to a solution of the ethoxyalanine in sodium hydroxide, separates from water in hexagonal plates and melts at 167—168° (corr.).

Ethoxyacetaldehydesemicarbazone,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , prepared by the addition of semicarbazide hydrochloride to ethoxyacetaldehyde ammonia (m. p. 79—81°), separates from water in rhombohedra and melts at 85—86°.

A. McK.

**Resolution of Racemic Serine into the Optically Active Components.** EMIL FISCHER and WALTER A. JACOBS (*Ber.*, 1906, 39, 2942—2950).—*p*-Nitrobenzoyl-*dl*-serine, prepared by the gradual addition of *p*-nitrobenzoyl chloride and potassium hydroxide to serine in the cold, crystallises from water in light yellow, thin needles, which sinter at 184° (corr.) and melt and decompose to a brown liquid at 206—207° (corr.). After heating with quinine in alcohol, the quinine salt of the *d*-compound separates on cooling and on hydrolysis yields *p*-nitrobenzoyl-*d*-serine, crystallising in glistening, faintly yellow plates which sinter at 171° (corr.) and melt at 189.5° (corr.). It has  $[\alpha]_D - 43.74^\circ$  at 20°. *d*-Serine, obtained from the foregoing on heating with hydrogen bromide, crystallises in large, colourless prisms or hexagonal plates which, on heating, become brown at 211° (corr.) and decompose about 228° (corr.). It has  $[\alpha]_D + 6.87^\circ$  at 20° in water and  $-14.32^\circ$  in *N*-hydrochloric acid and is approximately twice as soluble in water as racemic serine. The quinine salt of the *l*-compound is obtained from the mother liquors: to purify it, it is converted into the *brucine* salt, which crystallises in yellow prisms aggregated in rays. *p*-Nitrobenzoyl-*l*-serine is in every way similar to the *d*-compound, but has  $[\alpha]_D + 43.56^\circ$  at 20°. Similarly, *l*-serine has  $[\alpha]_D - 6.83^\circ$  at 20° in water and  $+14.45^\circ$  in *N*-hydrochloric acid. *d*-Serine has a definitely sweet taste; that of *l*-serine is less, although still appreciably sweet. *l*-Serine methyl ester was obtained as a colourless, strongly alkaline syrup; the hydrochloride consists of colourless four- or eight-sided microscopic plates decomposing at 167° (corr.). *l*-Serine anhydride forms slender, colourless needles melting and decomposing at 247° (corr.); it has  $[\alpha]_D - 67.46^\circ$  at 20°, and is identical with a product derived from silk fibroin. *l*-Serine is therefore regarded as the natural product.

The authors have also resolved *isoserine* and *diaminopropionic acid*. *Benzoylisoserine* has  $[\alpha]_D + 10.45^\circ$  at 20°, whilst the isomeric *dibenzoyl-diaminopropionic acids* show  $[\alpha]_D - 35.76^\circ$  and  $+35.9^\circ$  at 20° respectively.

E. F. A.

**Behaviour of Racemic Amino-acids towards Yeast.** New Biological Method for resolving them. FELIX EHRLICH (*Zeit. Ver. deut. Zuckerind.*, 1906, 608, 840—860).—Racemic amino-acids are readily attacked by yeast in solutions containing a large proportion of sucrose. The yeast should be poor in nitrogen and should be used in large excess, in order that the destruction of one of the component amino-acids may be complete. Any ordinary clean baker's yeast is

suitable, pure cultures of the pressed yeasts of Classes II and XII giving especially good results. These yeasts can now be procured very constant in composition, the dry matter they contain amounting to about 25 and the nitrogen to about 2 per cent.

Ten grams of the racemic amino-acid and from 200 to 300 grams of sucrose are dissolved in 2 to 3 litres of water contained in a capacious flask, and the solution, which need not be sterilised, mixed with a quantity of pressed yeast varying, for different amino-acids, from 50 to 150 grams. The flask is closed by means of a sulphuric acid seal and is vigorously shaken for some time. The fermentation is allowed to proceed at the ordinary temperature, since, if higher temperatures are employed, the autolytic activity of the yeast becomes greater, and an increased amount of the yeast-substance is thus introduced into the solution. When the liquid no longer reduces Fehling's solution or gives the naphthol reaction, the fermentation is complete; this is generally found to be the case after thirty-six to forty-eight hours, whilst in some cases twenty-four hours are sufficient. The clear liquid is syphoned off and the residual yeast placed on a large filter and washed with a little water. The whole of the solution is then mixed with a little alumina cream or kieselguhr and filtered, the clear liquid thus obtained giving no biuret reaction and only a faint Millon's reaction. The solution is boiled to a volume of 100—200 c.c., filtered, if necessary, after the addition of animal charcoal, and evaporated on the water-bath to a thin syrup. While the latter is cooling, crystallisation is started by scratching the dish with a glass rod.

If the specific rotation of the product indicates the presence of racemic compound, a second fermentation should be carried out in the same way as the first.

From the compounds examined by the author, namely, racemic alanine, leucine, and  $\alpha$ -aminoisovaleric acid, *l*-alanine, *d*-leucine, and *l*- $\alpha$ -aminoisovaleric acid were obtained in a pure state in yields amounting respectively to 65, 76, and 67 per cent. of the theoretical quantities. In all cases both optical isomerides are attacked by the yeast, but, as a rule, one far more rapidly than the other.

In hydrochloric acid solution, *d*-leucine has  $[\alpha]_D -15.4^\circ$  at  $20^\circ$  (compare Fischer and Warburg, this vol., i, 72).

When submitted to the action of yeast in the manner described, synthetical  $\alpha$ -amino- $\alpha$ -methylbutyric acid yields a laevorotatory compound, and, with a mixture of *d*-isoleucine and *d*-alloisoleucine, obtained either synthetically from *d*-amyl alcohol or by the action of barium hydroxide solution on natural *d*-isoleucine, the latter gives up its nitrogen to the yeast and is converted into *d*-amyl alcohol, whilst the *d*-alloisoleucine is not appreciably attacked. T. H. P.

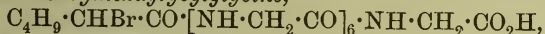
**Synthesis of Polypeptides. XV.** EMIL FISCHER (*Ber.*, 1906, 39, 2893—2931).— $\alpha$ -Bromoisohexoyltetraglycylglycyl chloride is prepared from bromoisohexoyltetraglycylglycine by the action of acetyl chloride and phosphorus pentachloride in the apparatus previously described (*Abstr.*, 1905, i, 863). The glycine must be specially prepared for chlorination by solution in cold alkali hydroxide and slow precipitation with hydrochloric acid and subsequent drying in a vacuum;



if crystallised from water or alcohol, the carboxyl group of the polypeptide resists all attempts at chlorination.

*α-Bromoisohexoyl-pentaglycylglycyl chloride* and *-hexaglycylglycyl chloride* are obtained as colourless solids in a similar manner.

*α-Bromoisohexoylhexaglycylglycine*,



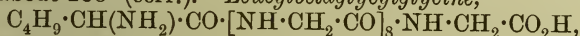
is prepared by condensation of triglycylglycine with *α-bromoisohexoyl-diglycylglycine chloride* in presence of sodium hydroxide, special experimental precautions being necessary to ensure success; it is obtained as a loose, colourless powder which, when quickly heated, turns yellow at about 245° (corr.) and melts and decomposes between 256° and 259° (corr.).

*Leucylhexaglycylglycine*,

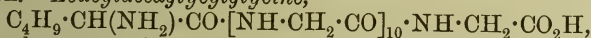


obtained by the action of liquid ammonia on the foregoing, is obtained as a microcrystalline, colourless powder with  $\text{H}_2\text{O}$  which, when rapidly heated, becomes yellow at about 200° and darkens and finally decomposes between 280° and 290°. It dissolves in hot hydrochloric acid, forming a sparingly soluble *hydrochloride*, and shows a marked biuret coloration.

*α-Bromoisohexyloctaglycylglycine* is prepared by coupling pentaglycylglycine with *α-bromoisohexoyldiglycylglycyl chloride* in presence of alkali; it turns yellow between 244° and 255° (corr.) and finally decomposes at about 288° (corr.). *Leucyloctaglycylglycine*,



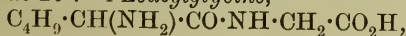
crystallises with  $\text{H}_2\text{O}$ , the dry substance being hygroscopic; it colours at 255° (corr.) and becomes black at 290° (corr.). *α-Bromoisohexoyl-decaglycylglycine* turns yellow at 230°, becomes brown above this, and black at about 293° (corr.); the alkaline solution gives a biuret coloration. *Leucyldecaglycylglycine*,



is a colourless, amorphous powder without a melting point; it shows a strong biuret coloration, is easily soluble in cold fuming hydrochloric acid, the *hydrochloride* being precipitated on dilution; the solution in dilute ammonia gives a dense precipitate with ammonium sulphate, and in this respect strongly resembles the natural proteids.

Active *α-bromoisohexoyldiglycylglycine*, prepared by condensation of diglycylglycine with *α-bromoisohexoyl chloride* from *d*-leucine, sinters at 163° (corr.) and melts at 168—169° (corr.) to a yellow liquid. In normal alkali it has  $[\alpha]_D + 31.98^\circ$  at 20°. *l-Leucyldiglycylglycine*,  $\text{C}_4\text{H}_9\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared by the action of aqueous ammonia on the preceding compound, forms stellar aggregates of glistening, prismatic crystals which, when quickly heated, become yellow at 220° (corr.) and melt at 230—232° (corr.), partially decomposing to a reddish-brown liquid. It has in aqueous solution  $[\alpha]_D + 45.85^\circ$  at 20° and gives a marked biuret coloration.

*d-α-Bromoisohexoylglycine*, prepared from *d-α-bromoisohexoic acid* and glycine, softens at 82° and melts at 85—86° (corr.). It crystallises in stellar aggregates of long needles from alcohol, in which solvent it has  $[\alpha]_D + 62.0^\circ$  at 20°. *l-Leucylglycine*,



sinters at  $235^{\circ}$  and melts at  $248^{\circ}$  (corr.), being partially converted into anhydride; it crystallises in needles and is more soluble in water than the racemic form; it tastes somewhat bitter, forms a deep blue copper salt, and has  $[\alpha]_D + 85.5^{\circ}$  at  $20^{\circ}$ .

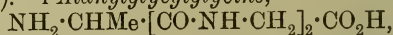
*l-Leucylglycine anhydride*,  $C_4H_9 \cdot CH \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} CH_2$ , prepared under special precautions from the ester of the dipeptide, sinters at  $245^{\circ}$  and melts at  $254-255^{\circ}$  (corr.); it tastes bitter, reacts neutral, and shows  $[\alpha]_D + 32.3^{\circ}$  at  $20^{\circ}$ . This anhydride is identical with a product obtained by Fischer and Abderhalden by the hydrolysis of elastin (this vol., i, 719).

*d- $\alpha$ -Bromoisohexoyl-d-alanine* crystallises in thin, long needles which soften at  $96^{\circ}$  and melt at  $101-103^{\circ}$  (corr.) and have  $[\alpha]_D + 23.0^{\circ}$  at  $20^{\circ}$ .

*l-Leucyl d-alanine*,  $C_4H_9 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CHMe \cdot CO_2H$ , forms flat, right-angled plates which taste bitter and melt at  $257^{\circ}$  (corr.); the copper salt crystallises in flat, blue prisms. The dipeptide dissolved in methyl alcohol gives  $[\alpha]_D + 23.7^{\circ}$  at  $20^{\circ}$ .  *$\alpha$ -Leucyl-d-alanine anhydride*,  $C_4H_9 \cdot CH \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} CHMe$ , crystallises in long needles melting at  $258^{\circ}$  (corr.), tastes bitter, and has  $[\alpha]_D - 29.0^{\circ}$  at  $20^{\circ}$ .

*d- $\alpha$ -Bromoisohexoyl-l-leucine* crystallises in microscopic, double pyramids, melting at  $149^{\circ}$  (corr.), and has  $[\alpha]_D + 16.2^{\circ}$  at  $20^{\circ}$ . *l-Leucyl-l-leucine*,  $C_4H_9 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot CO_2H$ , crystallises from water or alcohol in long, pointed plates aggregated in rosettes which melt at  $270^{\circ}$  (corr.) and have  $[\alpha]_D - 13.43^{\circ}$  at  $20^{\circ}$  in alkaline solution. It forms a crystalline *hydrochloride* and a blue *copper* salt separating in needles, and a characteristic *carbethoxy-l-leucyl-l-leucine*, of which the obliquely-cut plates melt at  $149-150^{\circ}$  (corr.) and are sparingly soluble even in hot water. *l-Leucine anhydride* (*l-leucineimide*), prepared from the methyl ester of the dipeptide, melts at  $277^{\circ}$  (corr.) and has  $[\alpha]_D - 42.8^{\circ}$  at  $20^{\circ}$ .

*l-Bromopropionylglycylglycine* crystallises in colourless prisms melting at  $172^{\circ}$  (corr.). *l-Alanylglycylglycine*,



forms colourless, centimetre long needles, belonging to the monoclinic, hemimorphous system, with  $H_2O$ , which become yellow at  $205^{\circ}$  and melt and decompose at  $245^{\circ}$  (corr.). It does not show a biuret coloration, and gives a precipitate with phosphotungstic acid. The aqueous solution has  $[\alpha]_D - 29.2^{\circ}$  at  $20^{\circ}$ . The *methyl* ester crystallises in colourless, glistening plates; it liquefies between  $90^{\circ}$  and  $95^{\circ}$ , and forms a *hydrochloride*, crystallising in bundles of needles, which melts at  $178^{\circ}$  (corr.). On heating at  $100^{\circ}$ , it is converted into the *ester* of the hexapeptide, a compound sintering at  $175^{\circ}$  and melting and decomposing at  $185^{\circ}$ , which gives a marked biuret coloration, and is hydrolysed by sodium hydroxide to *l-alanyldiglycyl-l-alanylglycylglycine*. This decomposes at  $207^{\circ}$  and has  $[\alpha]_D + 13^{\circ}$  at  $21^{\circ}$ .

*Triglycylglycine methyl ester*, prepared by esterifying the tetrapeptide with methyl alcohol and hydrogen chloride, crystallises in microscopic, glistening needles or thin sheaves of prisms: it becomes yellow at  $200^{\circ}$  and decomposes at  $240^{\circ}$ . The *hydrochloride* forms microscopic

platelets which melt at 198—200°. It gives a brilliant biuret coloration, and does not condense on heating to 100°.

Methods are described for preparing formyl *-d-*, *-l-*, and *-dl-*leucine, and the measurements of their rhombic crystals given. Better methods of preparing *d-a*-bromoisohexoic acid, *d-a*-bromoisohexoyl chloride, and glycine anhydride are also described.

E. F. A.

**Dithiocarbamoglycollic Acid** (Carboxymethyldithiourethane). B. HOLMBERG (*Ber.*, 1906, 39, 3068—3069. Compare Abstr., 1905, i, 323).—*Dithiocarbamoglycollic acid* (carboxymethyldithiourethane),  $\text{NH}_2\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is obtained when sulphuric acid is added to an aqueous solution of sodium chloroacetate and ammonium dithiocarbamate; it crystallises in needles or leaflets, darkens at 100°, and melts at 136—137°, yielding after a few minutes at the latter temperature the *anhydride*,  $\text{S} \begin{array}{c} \text{CS}-\text{NH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CO} \end{array}$ , which crystallises in large, yellow leaflets, melts and decomposes at 168—169°, and is also obtained by acidifying the mixture of sodium chloroacetate and ammonium dithiocarbamate with acetic acid, or in accordance with the equation  $\text{CH}_2\text{SH}\cdot\text{CO}_2\text{H} + \text{CS}(\text{NH}_2)_2 = \text{C}_3\text{H}_3\text{ONS}_2 + \text{NH}_3 + \text{H}_2\text{O}$ .

C. S.

**A New Group of Nitrogenous Carbohydrates.** TH. R. OFFER (*Beitr. chem. Physiol. Path.*, 1906, 8, 399—405. Compare Fränkel, Abstr., 1899, i, 396; Fränkel and Kelly, *ibid.*, 1902, i, 479).—A nitrogenous carbohydrate, which gives the pentose reactions, but reduces Fehling's solution after hydrolysis, has been isolated from horse's liver by extraction with alcohol after other substances had been removed by repeated extraction with acetone. Better yields are obtained by extracting the liver with hot water. After concentration of the clear extract, removal of proteids and glycogen, and further concentration and addition of methyl alcohol, a precipitate was obtained, which, after purification, was converted into its *copper* derivative,  $\text{C}_{10}\text{H}_{16}\text{O}_7\text{N}_2(\text{CuO})_2$ . The corresponding carbohydrate is probably a dipentosamine,  $2(\text{C}_5\text{H}_7\text{O}_3\cdot\text{NH}_2) + \text{H}_2\text{O}$ .

From the alcoholic filtrate, a *barium* compound,  $\text{C}_{14}\text{H}_{22}\text{O}_9\text{N}_2\text{Ba}$ , has been obtained; this corresponds with a *diacetylated* dipentosamine,  $\text{C}_{10}\text{H}_{18}\text{O}_7\text{N}_2\text{Ac}_2$ . The barium compound is readily soluble in water or alcohol, but insoluble in ether or methyl alcohol. It does not reduce Fehling's solution until boiled with hydrochloric acid, and gives the characteristic pentose reactions only after prolonged boiling.

J. J. S.

**Chloro-derivatives of Diacetamide.** HERMANN FINGER (*J. pr. Chem.*, 1906, [ii], 74, 153).—*Hexachlorodiacetamide*,  $\text{NH}(\text{CO}\cdot\text{CCl}_3)_2$ , prepared by heating trichloroacetonitrile with trichloroacetic acid in a sealed tube at 180—190°, crystallises from light petroleum, melts at 81°, and is decomposed by alcohol, forming ethyl trichloroacetate and trichloroacetamide, or by ammonia, forming 2 mols. of trichloroacetamide, or by prolonged heating at 120—140°, yielding trichloroacetonitrile, trichloroacetamide, and hexachloroacetic anhydride.

G. Y.

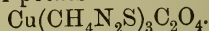


**Action of Sodium Hypobromite on some Amino-compounds.** J. STUHETZ (*Monatsh.*, 1906, 27, 601—605).—The action of sodium hypobromite on carbamide in aqueous solutions of different concentrations at the ordinary temperature and pressure leads to the evolution of 29·3—44·4 per cent. of nitrogen; the theoretical percentage, 46·6, was not evolved in any experiment.

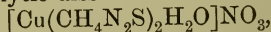
Glycine, alanine, leucine, glutamic acid, tyrosine, lysine, and histidine yield only very small quantities of nitrogen when treated with sodium hypobromite solution, whilst under the same conditions arginine evolves about 1/3 of its nitrogen. G. Y.

**Salts of Cuprothiocarbamides.** VOLKMAR KOHLSCHÜTTER and C. BRITTLEBANK (*Annalen*, 1906, 349, 232—268. Compare Rathke, *Abstr.*, 1884, 1017; Rosenheim and Loewenstamm, *Abstr.*, 1903, i, 325; Kohlschütter, *ibid.*, 468).—The greater part of this work has been published previously. The authors agree with Rosenheim and Stadler (this vol., i, 407) that the complex salts formed by thiocarbamide with cuprous chloride have the formulæ  $\text{Cu}(\text{CH}_4\text{N}_2\text{S})\text{Cl}_2$ ,  $\text{Cu}(\text{C}_6\text{H}_4\text{N}_2\text{S})_2\text{Cl}$ , and  $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{Cl}$ , the last on hydrolysis yielding the salt  $[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]\text{Cl}$ .

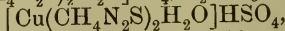
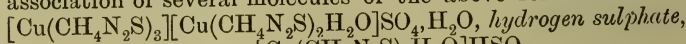
The complex compound,  $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{Cl}$ , is to be regarded as a salt of the univalent cation,  $[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3]^+$ , as on electrolysis with a current density of 0·02 ampere, the cathode vessel contains finally copper and thiocarbamide in the proportion 1:3·01; the abnormal conductivity results obtained with this salt are discussed and found to be in agreement with Kohlschütter's conclusions (*loc. cit.*). Contrary to Kohlschütter's statement, the oxalate formed on addition of oxalic acid to the chloride has the formula  $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{C}_2\text{HO}_4\cdot\text{H}_2\text{O}$ , whilst that formed by addition of potassium oxalate has the formula



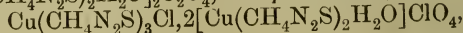
The salt  $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{NO}_3\cdot 4[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]\text{NO}_3$  crystallises in slender needles when dilute nitric acid is added to a saturated solution of the salt  $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_3\text{NO}_3\cdot [\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]\text{NO}_3$ . The comparison of the degree of electrolytic dissociation of the salt



$\alpha = 0\cdot39$  with  $v = 51\cdot3$ , with the molecular conductivity,  $\alpha = 0\cdot86$  with  $v = 32$ , shows that the part of the salt which is not electrolytically dissociated consists of polymeric molecules, and the solid salt is an association of several molecules of the above formula. The *sulphate*,



*oxalate*,  $[\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{H}_2\text{O}]_2\text{C}_2\text{O}_4$ , and *perchlorate*,



are described.

The solubility of thiocarbamide in water increases on addition of cuprothiocarbamide chloride in proportion to the amount of the chloride added; similarly, the solubility of the chloride in water is increased by the presence of thiocarbamide, showing that a further addition of thiocarbamide to the cuprotrithiocarbamide takes place, which is in agreement with the results of the cryoscopic mol. weight determination.

Cuprodithiocarbamide chloride,  $\text{Cu}(\text{CH}_4\text{N}_2\text{S})_2\text{Cl}$ , formed by the action of potassium chloride on cuproaquodithiocarbamide nitrate, is a salt of the type of triaminocobalt nitrite, and is only very slightly dissociated.

The bearing of the behaviour of cuprodithiocarbamide chloride on the theory of the influence of the anion on the formation of complex cations is discussed.

Cuprothiocarbamide chloride,  $\text{Cu}(\text{CH}_4\text{N}_2\text{S})\text{Cl}$ , which occurs in two modifications, resembles cuprous chloride in its behaviour, dissolving in concentrated hydrochloric acid and, although less readily, in saturated sodium chloride solution; the solution in hydrochloric acid absorbs carbon monoxide. On electrolysis of the cupro-chloride in hydrochloric acid solution, the amount of thiocarbamide at the cathode diminishes in consequence of the wandering of anions containing thiocarbamide.

G. Y.

*iso*Butylhydantoic Acid and Detection of Small Quantities of Leucine. FRITZ LIPPICH (*Ber.*, 1906, 39, 2953—2956).—Baumann and Hoppe-Seyler formerly observed that hydantoic acid was produced when a solution of glycine and carbamide was boiled with baryta water until the evolution of ammonia ceased. Similarly, Pinner and Spilker (*Abstr.*, 1889, 704) prepared *isobutylhydantoin* from *isovaleraldehyde* hydrocyanide and carbamide, and thence obtained the *isobutylhydantoic acid* corresponding with leucine by boiling with baryta water. It is probable that the reaction (the formation of hydantoic acids) is general for all the  $\alpha$ -aminocarboxylic acids, and a preliminary experiment with aminovaleric acid has confirmed this supposition. The reaction may be used to detect small quantities of leucine in a mixture of other amino-acids. For example, a mixture of 1 gram of leucine, 0.5 gram of glycine, and 0.5 gram of tyrosine was boiled with carbamide and baryta water in moderate excess until the evolution of ammonia had ceased, the excess of barium was removed by carbon dioxide, and the filtrate cautiously acidified with acetic acid. The crystalline precipitate thus obtained was recrystallised from 50 per cent. alcohol, when the substance separated in aggregates of well-defined, colourless needles melting at  $205^\circ$ . The properties of this substance show that it is identical with Pinner and Spilker's *isobutylhydantoic acid*. On account of the sparing solubility of the free *isobutylhydantoic acid* and the great solubility of its crystallisable barium salt, this reaction may be generally applied to the detection of leucine, and as little as 0.01 gram of the pure amino-acid may be distinguished in this way.

G. T. M.

Specific Rotation of Glutamine. ERNST SCHULZE (*Ber.*, 1906, 39, 2932—2933. Compare *Abstr.*, 1885, 759).—Seven preparations of glutamine from various vegetable sources were found to have  $[\alpha]_D$  between  $+1.9^\circ$  and  $+9.5^\circ$ , the differences being probably due to the preparations containing the two stereoisomerides in varying proportions.

E. F. A.

**Complex Compounds of Organic Imides. Succinimide Nickel Derivatives.** LEO TSCHUGAEFF (*Ber.*, 1906, 39, 3190—3201. Compare Abstr., 1904, i, 478; 1905, i, 865).—The succinimide nickel group,  $(\text{Su})_2\text{Ni}$  [ $\text{Su} = \text{C}_2\text{H}_4(\text{CO})_2\text{N}$ ], combines with aliphatic monoamines to form a series of compounds,  $(\text{Su})_2\text{Ni}, 2a$  [ $a = \text{an amine}$ ], which resemble in general character the copper compounds already described. The compounds in question are prepared according to two methods: (1) Interaction of nickel salts and amines in presence of a slight excess of succinimide, the action, which is conducted in alcoholic solution, being in accordance with the scheme  $\text{NiX}_2 + 2\text{SuH} + 4a = \text{Ni}(\text{Su})_2, 2a + 2a, \text{HCl}$ . (2) Action of amines on nickel succinimide octahydrate, the reaction taking place either at the ordinary temperature or on gentle warming in the presence of a little alcohol, thus:  $(\text{Su})_2\text{Ni}, 8\text{H}_2\text{O} + 2a = (\text{Su})_2\text{Ni}, 2a + 8\text{H}_2\text{O}$ .

The compounds  $(\text{Su})_2\text{Ni}, 2a$  form yellow needles, and undergo no change when kept under diminished pressure over sulphuric acid. They are also moderately stable towards heat, and begin to decompose above  $200^\circ$ . Solutions in water and in alcohol are bluish-green and unstable. Aqueous solutions readily undergo hydrolytic dissociation, with separation of nickelous hydroxide. The compounds are readily decomposed by acids, thus:  $(\text{Su})_2\text{Ni}, 2a + 4\text{HX} = 2\text{SuH} + 2a\text{HX} + \text{NiX}_2$ . The following compounds are described: *methylamine* compound,  $(\text{Su})_2\text{Ni}, 2\text{Me}\cdot\text{NH}_2$ ; *propylamine* compound,  $(\text{Su})_2\text{Ni}, 2\text{Pr}\cdot\text{NH}_2$ ; *isobutylamine* compound,  $(\text{Su})_2\text{Ni}, 2\text{C}_4\text{H}_9\cdot\text{NH}_2$ ; *allylamine* compound,  $(\text{Su})_2\text{Ni}, 2\text{C}_3\text{H}_5\cdot\text{NH}_2$ ; *camphylamine* compound,  $(\text{Su})_2\text{Ni}, 2\text{C}_{10}\text{H}_{17}\cdot\text{NH}_2, 2\text{H}_2\text{O}$ ; the latter forms lilac needles.

The only compound obtained from a secondary amine was a yellow, crystalline, very unstable compound from dimethylamine and the octahydrate, whilst tertiary amines do not form double compounds with succinimide.

When an excess of succinimide is added to a concentrated solution of nickel chloride or of nickel acetate, and trimethylamine is then added to the warm solution, the *octahydrate*,  $(\text{Su})_2\text{Ni}, 8\text{H}_2\text{O}$ , separates as bright blue needles.

*Triethylenediamine nickel succinimide*,  $\text{C}_{14}\text{H}_{32}\text{O}_4\text{N}_8\text{Ni}, 2\text{H}_2\text{O}$ , prepared by the action of ethylenediamine on the octahydrate, crystallises in reddish-violet prisms. It decomposes at about  $200^\circ$ . Its aqueous solutions are reddish-violet.

Propylenediamine and butylenediamine also react with the octahydrate. The compound  $\text{C}_8\text{H}_{20}\text{N}_6\text{S}_2\text{Ni}$  is formed when potassium thiocyanate is added to the solution obtained by the addition of trimethylenediamine to the octahydrate; it crystallises in lilac needles or prisms.

The action of tetramethylenediamine and pentamethylenediamine respectively on the octahydrate was also studied, but well-defined compounds were not obtained.

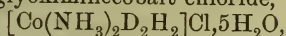
A. McK.

**Cobalt Dioximines.** LEO TSCHUGAEFF (*Ber.*, 1906, 39, 2692—2702. Compare Abstr., 1904, i, 478; 1905, i, 743, 865).—The ammine derivatives of the dioximines can be formulated in accordance with Werner's



theory, the complex  $D_2H_2$  (where  $D = \begin{smallmatrix} R \cdot C \cdot NO \cdot \\ | \\ R \cdot C \cdot NO \cdot \end{smallmatrix}$ ) occupying four positions in the metallic complex. Moreover, the ammonia can be replaced by methylamine, ethylamine, or pyridine.

Diamminedimethylglyoximinecobalt chloride,



is obtained (1) by heating dimethylglyoxime, chloropentamminecobalt chloride (purpureochloride), and a solution of ammonium acetate on the water-bath; (2) in a similar manner from hexamminecobalt chloride (luteochloride), dimethylglyoxime, and excess of ammonium acetate; (3) from carbonatotetramminecobalt sulphate as in (2), excess of potassium or ammonium chloride being added to precipitate the chloride; (4) by passing air through a concentrated solution of cobaltous chloride, dimethylglyoxime, and excess of 10 per cent. ammonium hydroxide, ammonium chloride being finally added after the solution has been evaporated to a small bulk.

*Chloroamminedimethylglyoximinecobalt*,  $[CoCl(NH_3)D_2H_2]$ , is obtained when the first-mentioned method of preparation is carried out in the presence of acetic acid; it crystallises in dark brown needles or prisms, is stable to acids or alkalis, does not contain ionisable chlorine, and consequently does not possess electrical conductivity. Concentrated sulphuric acid dissolves the substance, forming a rose-red solution, which evolves hydrogen chloride only when heated strongly. The substance is converted into the preceding chloride by treatment with ammonium hydroxide.

*Nitritoamminedimethylglyoximinecobalt*,  $[Co(NO_2)(NH_3)D_2H_2]$ , obtained from xantho- or isoxantho-cobalt chloride, separates from hot water in small, yellowish-brown prisms. The nitrite group is not ionisable.

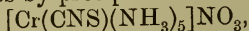
*Diethylaminedimethylglyoximinecobalt chloride*,  $[Co(NH_2Et)_2D_2H_2]Cl$ , results when air is passed for four to five hours through a solution of cobalt chloride, dimethylglyoxime, and ethylamine. It separates from hot water in small, brownish-yellow prisms or plates, and is very soluble in water. Potassium iodide or nitrate or sodium chlorate precipitate the corresponding sparingly soluble salts. The *iodide* separates from 30–40 per cent. alcohol in golden-yellow needles; the *nitrate* crystallises from hot water. The *base*,  $[Co(NH_2Et)_2D_2H_2] \cdot OH$ , obtained from the chloride and silver oxide, is only stable in solution; it has an alkaline reaction, absorbs carbon dioxide from the atmosphere, precipitates the hydroxides of the heavy metals, and with acids yields the corresponding salts. The solution has a yellowish-brown colour and does not smell of ethylamine.

*Dipyridinedimethylglyoximinecobalt chloride*,  $[Co(C_5NH_5)_2D_2H_2]Cl$ , obtained in 50 per cent. alcoholic solution in a similar manner to the ethylamine compound, separates in large, dark brown crystals. When it is dissolved in warm water and treated with a slight excess of potassium hydroxide, the *anhydro-base*,  $[Co(C_5NH_5)_2D_2H_2]$ , is obtained quantitatively as a dark brown, crystalline precipitate. The *nitrate*,  $[Co(C_5NH_5)_2D_2H_2]NO_3$ , obtained by dissolving the anhydro-base in dilute nitric acid, forms brown, nacreous leaflets, is electrolytically

dissociated in aqueous solution, and yields, with potassium iodide or thiocyanate, precipitates of the corresponding salts. C. S.

### Thiocyanoamminechromium Salts. VI. Chromium Salts.

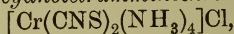
ALFRED WERNER and J. VON HALBAN (*Ber.*, 1906, 39, 2668—2673. Compare this vol., ii, 452).—*Thiocyanopentamminechromium thiocyanate*,  $[\text{Cr}(\text{CNS})(\text{NH}_3)_5]\cdot\text{CNS}$ , is obtained when chloropentamminechromium chloride (compare Christensen, *Abstr.*, 1893, ii, 469) is boiled with an excess of a concentrated acetic acid solution of potassium thiocyanate; it separates in aggregates of orange or reddish-brown leaflets, is easily soluble in hot water, has not been obtained pure, and yields the following salts by precipitation. The *nitrate*,



separates from dilute acetic acid in orange-yellow crystals; the *dichromate*,  $[\text{Cr}(\text{CNS})(\text{NH}_3)_5]\text{Cr}_2\text{O}_7$ , crystallises in bronze-coloured needles; the *chloride*,  $[\text{Cr}(\text{CNS})(\text{NH}_3)_5]\text{Cl}_2$ , is very stable to concentrated hydrochloric acid; the *bromide*,  $[\text{Cr}(\text{CNS})(\text{NH}_3)_5]\text{Br}_2$ , crystallises in deep orange crystals.

*Nitratopentamminechromium nitrate*,  $[\text{Cr}(\text{NO}_3)(\text{NH}_3)_5](\text{NO}_3)_2$ , is obtained from concentrated nitric acid, and the preceding nitrate or the aquopentamminechromium base derived from the chloropentamminechromium chloride; it is sparingly soluble in cold water, and at 30—40° the colour of the solution changes from red to violet, and the nitrate-salt cannot be recovered. The *iodide*,  $[\text{Cr}(\text{NO}_3)(\text{NH}_3)_5]\text{I}_2$ , is obtained from the nitrate and potassium iodide.

When thiocyanopentamminechromium thiocyanate is heated at 130—140°, until the evolution of ammonia ceases, a mixture is obtained from which *dithiocyanotetramminechromium chloride*,



and *trithiocyanotriamminechromium*,  $\text{Cr}(\text{CNS})_3(\text{NH}_3)_3$ , have been isolated. The latter is insoluble in cold water, alcohol, ether, or chloroform, but dissolves in piperidine, quinoline, benzylamine, acetonitrile, or acetone, being reprecipitated by the addition of ether. C. S.

**Insoluble Chromicyanides.** FREDERICK VAN DYKE CRUSER and EDMUND H. MILLER (*J. Amer. Chem. Soc.*, 1906, 28, 1132—1151).—Potassium chromicyanide,  $\text{K}_3\text{Cr}(\text{CN})_6$ , was prepared by a modification of Christensen's method (*Abstr.*, 1885, 737). The following salts were obtained as insoluble precipitates by adding solution of potassium chromicyanide to solutions of metallic salts.

*Cadmium chromicyanide*,  $\text{Cd}_3\text{Cr}_2(\text{CN})_{12}$ , forms a white precipitate with a slightly green tinge. *Cobalt chromicyanide*,  $\text{Co}_3\text{Cr}_2(\text{CN})_{12}$ , is obtained as a light rose-coloured precipitate which becomes yellowish-brown on drying. *Cuprous chromicyanide*,  $\text{Cu}_3\text{Cr}(\text{CN})_6$ , forms an orange-yellow precipitate. *Cupric chromicyanide*,  $\text{Cu}_3\text{Cr}_2(\text{CN})_{12}$ , is blue when first precipitated, but gradually becomes green, and when dry is reddish-purple. *Ferrous chromicyanide*,  $\text{Fe}_3\text{Cr}_2(\text{CN})_{12}$ , is obtained as a brick-red, granular precipitate, which, on drying, becomes dark green. *Manganous chromicyanide*,  $\text{Mn}_3\text{Cr}_2(\text{CN})_{12}$ , forms a greenish-white, crystalline precipitate, and when dry is of a light brown colour. *Nickel chromicyanide*,  $\text{Ni}_3\text{Cr}_2(\text{CN})_{12}$ , forms a light greenish-blue precipitate which becomes black on drying. *Silver*

*chromicyanide*,  $\text{Ag}_3\text{Cr}(\text{CN})_6$ , is obtained as an orange-yellow precipitate, and when dry is rose-red in colour. *Zinc chromicyanide*,  $\text{Zn}_3\text{Cr}_2(\text{CN})_{12}$ , forms a yellowish-white, crystalline precipitate which becomes straw-coloured on drying.

On adding potassium chromicyanide solution to mercurous nitrate solution, a yellowish-white precipitate is produced, which rapidly darkens and finally becomes grey. It is probable that the original precipitate consists of mercurous chromicyanide, which decomposes with formation of mercurous cyanide, the latter becoming converted into mercuric cyanide and mercury.

The action of various reagents, such as the mineral acids, alkali hydroxides, and sodium peroxide, on these insoluble chromicyanides is described.

Solutions of lead acetate and nitrate of *N*/10 strength do not yield precipitates with *N*/10 potassium chromicyanide. A list is given of a large number of other salts which also fail to give a precipitate with this reagent.

E. G.

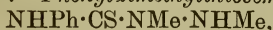
**Reactions at Low Temperatures. I. Cyanides.** WALTER PETERS (*Ber.*, 1906, 39, 2782—2784).—The compounds described were prepared by dissolving separately the base and hydrogen cyanide in absolute ether, cooling to  $-70^\circ$ , and then mixing.

*Diethylammonium cyanide* is colourless, soluble in alcohol, and decomposes between  $-20^\circ$  and  $-30^\circ$ . *Triethylammonium cyanide* crystallises in needles and decomposes between  $-40^\circ$  and  $-50^\circ$ . *Dimethylhydrazinium cyanide* also crystallises in needles, decomposing between  $-6^\circ$  and  $-10^\circ$ . *Pentamethylenediaminium cyanide* soon becomes sticky, and decomposes from  $-40^\circ$  to  $-50^\circ$ . *Piperidinium cyanide* decomposes from  $-25^\circ$  to  $-35^\circ$ , whilst *coniinium cyanide* decomposes at about  $-40^\circ$  to  $-50^\circ$ .

E. F. A.

***s*-Dimethylhydrazine.** LUDWIG KNORR and A. KÖHLER (*Ber.*, 1906, 39, 3257—3265).—When 1-methylpyrazole methiodide (obtained quantitatively from pyrazole, methyl alcohol and methyl iodide) is heated with a concentrated solution of potassium hydroxide, formic acid and a basic oil are produced; the latter has not been thoroughly examined, but from it *s*-dimethylhydrazine has been isolated. It boils at  $81^\circ$  under 747 mm. pressure, has a sp. gr. 0.8274 and  $n_D$  1.4209 at  $20^\circ$  (compare Harries and Klamt, *Abstr.*, 1895, i, 262). The *acid hydrochloride*, *acid sulphate*, and *acid oxalate*, and the *picrate* and *picrolonate*, are described.

*Dimethylsemicarbazide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NMe}\cdot\text{NHMe}$ , obtained from *s*-dimethylhydrazine, hydrochloric acid, and potassium cyanate, melts at  $116^\circ$ . *s*-Dicarbanilyldimethylhydrazine,  $\text{N}_2\text{Me}_2(\text{CO}\cdot\text{NHPh})_2$ , obtained from phenylcarbimide and the base in ethereal solution, melts and decomposes at  $288^\circ$ . *Phenyldimethylthiosemicarbazide*,



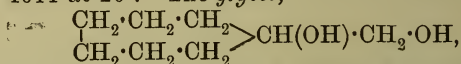
melts at  $115^\circ$ . *s*-Dibenzoyldimethylhydrazine,  $\text{NMeBz}\cdot\text{NMeBz}$ , obtained by the Schotten-Baumann method, melts at  $85^\circ$ . *Dimethylpicrazide*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{NMe}\cdot\text{NHMe}$ , obtained from *s*-dimethylhydrazine and picryl chloride in alcoholic solution, melts at  $141^\circ$ .

C. S.



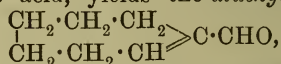
**Explanation of the Substitution of Aromatic Compounds.** ARNOLD F. HOLLEMAN (*J. pr. Chem.*, 1906, [ii], 74, 157—160. Compare Abstr., 1903, i, 623).—An amplification of the author's criticisms of Flürscheim's theory of substitution in the aromatic series (Abstr., 1903, i, 79; 1905, i, 614; this vol., ii, 529). G. Y.

**The Simplest Methylene Hydrocarbons of Various Ring Systems and their Conversion into Alicyclic Aldehydes.** OTTO WALLACH [with H. KÖHLER] (*Chem. Centr.*, 1906, ii, 602; from *Nachr. k. Ges. Wiss. Göttingen*, 1906, 74—80. Compare this vol., i, 553).—*Methylenecycloheptane* boils at 138—140°, has a sp. gr. 0·824 at 20°, and  $n_D = 1·4611$  at 20°. The *glycol*,



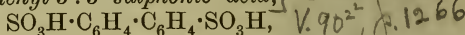
obtained from it melts at 50—51° and boils at 135—140°; on warming with dilute sulphuric acid, it yields suberanaldehyde,  $\text{C}_8\text{H}_{14}\text{O}$ , the semicarbazone of which melts at 153—154°.

When hydrochloric acid is removed from the nitrosochloride of methylenecycloheptane, a liquid oxime is obtained which, when warmed with dilute sulphuric acid, yields the *aldehyde*,



the *semicarbazone* of which melts at 203—204°. When oxidised by means of silver oxide, the aldehyde is converted into suberenecarboxylic acid, which melts at 50—51°. H. M. D.

**Constitution of Griess' Benzidinedisulphonic Acid.** GUSTAV SCHULTZ and W. KOHLHAUS (*Ber.*, 1906, 39, 3341—3345. Compare Griess, Abstr., 1881, 428; Griess and Duisberg, Abstr., 1890, 57).—Griess' benzidinedisulphonic acid is 4:4'-diaminodiphenyl-3:3'-disulphonic acid, as on elimination of the amino-groups by diazotisation and treatment of the product with copper powder in alcoholic solution it yields [*diphenyl-3:3'-sulphonic acid*], *See supra*



which on fusion with potassium hydroxide is converted into Haeussermann and Teichmann's 3:3'-dihydroxydiphenyl (Abstr., 1894, i, 598).

The 3:3'-disulphonic acid is obtained as a syrup; it is isolated in the form of its *potassium* salt,  $\text{C}_{12}\text{H}_8\text{O}_6\text{S}_2\text{K}_2 \cdot 2\text{H}_2\text{O}$ , which crystallises in almost colourless leaflets and is readily soluble in alcohol or water.

*Diphenyl-3:3'-disulphonyl chloride*,  $\text{C}_{12}\text{H}_8(\text{SO}_2\text{Cl})_2$ , crystallises from chloroform in colourless needles, and melts at 127·5—128°; the 3:3'-disulphonamide,  $\text{C}_{12}\text{H}_8(\text{SO}_2 \cdot \text{NH}_2)_2$ , crystallises in stellate aggregates of microscopic needles and melts at 285°; the 3:3'-disulphonanilide,  $\text{C}_{12}\text{H}_8(\text{SO}_2 \cdot \text{NHPh})_2$ , crystallises in glistening, prismatic, almost colourless prisms and melts at 181·5°. *Methyl diphenyl-3:3'-disulphonate*,  $\text{C}_{12}\text{H}_8(\text{SO}_3\text{Me})_2$ , crystallises in white needles and melts at 132·5°. 3:3'-Dihydroxydiphenyl crystallises in needles and gives a bluish-violet coloration with ferric chloride. The

*dibenzoate*,  $C_{12}H_8(OBz)_2$ , crystallises in white needles and melts at  $92^\circ$ . G. Y.

**Benzylsulphinic Acid and Dibenzylsulphoxide.** EMIL FROMM and JOSÉ DE SEIXAS PALMA (*Ber.*, 1906, 39, 3308—3317. Compare Otto and Lueders, *Abstr.*, 1880, 811).—Dibenzylsulphone is formed always as an impurity in the preparation of benzylsulphinic acid.

In aqueous solution at the ordinary temperature, sodium benzylsulphonate undergoes slight decomposition, yielding small quantities of benzaldehyde; at higher temperatures, benzoic acid, stilbene, sulphur, and thionessal are formed. Benzylsulphinic acid, prepared by the action of hydrogen sulphide on lead benzylsulphonate, crystallises in needles, is unstable in aqueous solution, being readily hydrolysed to sulphur dioxide and benzaldehyde, and reduces iodine; when treated with methyl iodide and sodium hydroxide, it forms benzylmethylsulphone.

*Dibenzylsulphoxide*,  $CH_2Ph \cdot SO \cdot SO \cdot CH_2Ph$ , is formed by the decomposition of benzylsulphinic acid in aqueous solution. It crystallises in prisms, melts at  $108^\circ$ , is neutral, does not reduce iodine, and when treated with methyl iodide and potassium hydroxide yields benzylmethylsulphone; when boiled with benzyl chloride and sodium hydroxide, it forms dibenzylsulphone and dibenzylsulphoxide.

*Benzylsulphonanilide*,  $CH_2Ph \cdot SO_2 \cdot NHPh$ , crystallises in white needles melting at  $103^\circ$ ; the *p*-toluidide,  $C_{14}H_{15}O_2NS$ , forms white prisms melting at  $113^\circ$ ; the *o*-phenetide,  $C_{15}H_{17}O_3NS$ , crystallises in white prisms and melts at  $85^\circ$ .

*Sodium and lead benzylsulphinates* are formed by reduction of benzylsulphonyl chloride with zinc dust and alcohol; they decolorise iodine, but not indigotin, and when boiled with alkyl haloids form benzylalkylsulphones.

*Benzylmethylsulphone*,  $CH_2Ph \cdot SO_2Me$ , crystallises in long needles and melts at  $127^\circ$ .

*Benzylethylsulphone*,  $CH_2Ph \cdot SO_2Et$ , forms scales or needles and melts at  $84^\circ$ . G. Y.

**Oxides of Hydrogen Sulphide.** EMIL FROMM and JOSÉ DE SEIXAS PALMA (*Ber.*, 1906, 39, 3317—3326).—When boiled with sodium hyposulphite and a trace of zinc dust in 30 per cent. aqueous sodium hydroxide, benzyl chloride yields dibenzylsulphone and sodium benzylsulphonate; the hyposulphite reacts therefore as a mixture of a sulphite and a sulphyxylate. The action of sodium hyposulphite on benzyl chloride in 50 per cent. aqueous sodium hydroxide at the ordinary temperature leads to the formation of sodium benzylsulphinate, which is identified by conversion into benzylmethylsulphone (compare preceding abstract).

Zinc dust reacts with sulphuryl chloride in ethereal solution, forming zinc chloride and *zinc sulphyxylate*,  $ZnSO_2$ , which is converted into dibenzylsulphone when heated with benzyl chloride and 10 per cent. sodium hydroxide; benzylsulphonic acid is not formed, as would be the case were the product of the sulphuryl chloride reaction zinc hypo-

sulphite. The syrupy product obtained on evaporating the ethereal solution of the sulfoxylate reduces indigotin.

Attempts were made to prepare sulphur hydrate,  $\text{H}_2\text{SO}$ , the hypothetical parent substance of the organic sulphoxides, which lies between hydrogen peroxide and hydrogen persulphide.

The action of thionyl chloride on zinc dust leads to the formation of zinc chloride, sulphur dioxide, and sulphur; a sulphoxide is not formed by treating the mixed products with benzyl chloride.

Benzyl disulphide, sulphide, and mercaptan are formed by the action of benzyl chloride on the product of the oxidation of sodium sulphide by hydrogen peroxide.

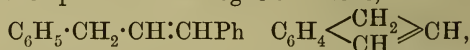
Sodium sulphide is oxidised to only a small extent by the hypochlorite yielding sodium sulphate.

The action of sulphur on potassium hydroxide and treatment of the product with benzyl chloride leads to the formation of thiobenzoic and benzoic acids together with a small amount of benzyl disulphide.

Thiobenzoic acid is oxidised to benzoyl disulphide by potassium ferricyanide in alkaline solution. G. Y.

**9-Ethylphenanthrene.** ROBERT PSCHORR (*Ber.*, 1906, 39, 3128—3129).—9-*Phenanthrylmethylcarbinol*,  $\text{C}_{14}\text{H}_9\cdot\text{CHMe}\cdot\text{OH}$ , resulting from acetaldehyde and 9-bromophenanthrene by the Grignard method, melts at  $137^\circ$  (corr.), and forms an *acetate*,  $\text{C}_{19}\text{H}_{18}\text{O}_2$ , which melts at  $100^\circ$  and boils at  $230\text{--}235^\circ$  under 12 mm. pressure. By distillation with zinc dust, the carbinol yields 9-*ethylphenanthrene*,  $\text{C}_{16}\text{H}_{14}$ , which melts at  $61\text{--}63^\circ$ , forms a *picrate* melting at  $124^\circ$ , and by oxidation with chromic acid yields phenanthraquinone. C. S.

**$\alpha\gamma$ -Diphenylpropylene.** WALTER DIECKMANN and HERMANN KÄMMERER (*Ber.*, 1906, 39, 3046—3051).— $\alpha\gamma$ -Diphenylpropylene may be regarded as the open chain analogue of indene,



and accordingly it has been studied with the view of ascertaining how far the capacity for condensation exhibited by indene, fluorene, and *cyclopentadiene*, and due to the neighbouring ethylene linkings present in these substances, would be recognisable in open chain compounds of similar constitution. The anticipation that the methylene group of  $\alpha\gamma$ -diphenylpropylene would have the same reactivity as that in indene has not been confirmed; the results tend to show that the reactivity of the double linking is increased by the cyclic structure.

$\alpha\gamma$ -Diphenylpropylene may be prepared from benzylcinnamic acid, obtained by condensing benzaldehyde and dihydrocinnamic acid; this is heated at  $100^\circ$  with a saturated glacial acetic acid solution of hydrogen bromide, when  $\beta$ -bromodibenzylacetic acid is formed, which crystallises from glacial acetic acid in colourless, lustrous needles melting at  $191\cdot5^\circ$ . This acid is converted quantitatively into  $\alpha\gamma$ -diphenylpropylene by warming with excess of aqueous sodium hydroxide. The hydrocarbon thus obtained, which boils at  $178\text{--}179^\circ$  under 15 mm. pressure, is a colourless liquid with the fragrant odour of hyacinths; its molecular weight corresponds with



the formula  $C_{15}H_{14}$ . It is probably a stereoisomeride of the solid hydrocarbon (m. p.  $57^\circ$ ) obtained by Francis (Trans., 1899, 75, 869), as the oily hydrocarbon gives a *dibromide* melting at  $110^\circ$ , whilst that derived from the solid hydrocarbon melts at  $231^\circ$ .

The hydrocarbon may be prepared also from  $\alpha\gamma$ -diphenyl- $\alpha$ -propanol or from  $\alpha\gamma$ -diphenyl- $\beta$ -propanol by conversion into the crude chlorides, which are then heated with diethylaniline, or preferably with pyridine.

$\alpha\gamma$ -Diphenylpropylene does not condense with ethyl oxalate or diazo-compounds, benzaldehyde or cinnamaldehyde, and it does not develop any coloration with ferric chloride. It is not affected by ethyl nitrite and sodium in dry ethereal solution. When oxidised with permanganate, either in aqueous or acetone solution, it furnishes benzoic, phenylacetic, and benzoylformic acids, the last two being formed in relatively small proportions.

G. T. M.

**Preparation of Triphenylmethane by the Action of Chloroform or Benzylidene Chloride on Magnesium Phenyl Bromide.** ALBERT REYCHLER (*Bull. Soc. chim.*, 1906, [iii], 35, 737—740).—When chloroform, dissolved in ether, is added to magnesium phenyl bromide dissolved in ether, and the liquid is treated in the usual way, a yield of triphenylmethane equivalent to from 70—80 per cent. of the theoretical is obtained. When chloroform is replaced by benzylidene chloride in this reaction, some tetraphenylmethane is produced in addition to triphenylmethane.

Carbon tetrachloride reacts very violently with magnesium phenyl bromide. Benzenyl trichloride also reacts energetically, forming a crystalline precipitate which, submitted to the usual treatment, yields only a sticky product. Commercial methylene dichloride also reacts with magnesium phenyl bromide, yielding triphenylmethane, but this is probably entirely due to the chloroform present in the commercial article. Chloroform reacts with magnesium ethyl bromide, yielding a colourless precipitate.

T. A. H.

**Triphenylmethyl.** XIV. MOSES GOMBERG and LEE H. CONE (*Ber.*, 1906, 39, 2957—2970. Compare this vol., i, 414).—The  $\alpha\beta\beta\beta$ -Tetra-phenylethane prepared by the authors' method was found to be identical in all respects with the product formerly obtained by Hanriot and Saint-Pierre (*Abstr.*, 1889, 882); the pure hydrocarbon may be distilled under reduced pressure, when it boils at  $277$ — $280^\circ$  under 21 mm. pressure.

$aaa$ -Triphenylpropane, formerly obtained as an oil, has now been caused to solidify by sowing with a crystal of the next homologue, triphenylbutane; after crystallisation from methyl alcohol, it melts at  $51^\circ$ .

It was also shown that the oily products obtained by E. and O. Fischer (*Annalen*, 1878, 194, 259), and by Hanriot and Saint-Pierre (*loc. cit.*), contain crystallisable  $aaa$ -triphenylpropane.

$aaa$ -Triphenylbutane, prepared by the interaction of magnesium propyl bromide and triphenylmethyl chloride, propylene and triphenylmethane being obtained as by-products, crystallises from methyl or ethyl alcohol in fine needles or in hexagonal plates; both forms melt at  $79^\circ$ , and the substance boils at  $262$ — $265^\circ$  under 62 mm. pressure.

When *aaa*-triphenylethane is prepared by the interaction of triphenylmethyl chloride and magnesium methiodide, no gaseous olefine was evolved, as in the case of magnesium ethyl or propyl haloid, and the yield of the product was 70 per cent. of the calculated amount.

*aaa-Triphenylisobutane*, produced from magnesium isopropyl bromide and triphenylmethyl chloride, boils at 233—234° under 21 mm. pressure, and has not been solidified.

*aaa-Triphenylisohexane*, prepared from magnesium isoamyl bromide and triphenylmethyl chloride, is a viscid, pale yellow, highly refractive oil having an intense blue fluorescence.

The hydrocarbons of this series can all be nitrated with excess of fuming nitric acid until the number of entrant nitro-groups corresponds with the number of phenyl nuclei in the molecule, but in some cases the nitration must be repeated before this result is attained. All the nitrohydrocarbons, with the exception of trinitrotriphenylbutane, give the magenta reaction, and are therefore probably tri-*para*-derivatives. Two isomeric *tetranitro-as-tetraphenylethanes* were obtained, a more soluble substance present only in small quantities and melting at 258°, and the less soluble main product which melts at 269°.

*Trinitro-aaa-triphenylpropane*, obtained after repeated nitration of the hydrocarbon, crystallises from glacial acetic acid in pale yellow plates and melts at 194—195°.

*Trinitro-aaa-triphenylbutane* crystallises from glacial acetic acid and melts at 191—192°. *Trinitro-aaa-triphenylisobutane* melts at 262—263°. *Trinitro-aaa-triphenylisohexane* crystallises in prisms, melts at 207—208°, and, like the foregoing nitro-derivative, it dissolves sparingly in glacial acetic acid.

The compound from phenyldiphenylenechloromethane, described in the last communication as a hydrocarbon (this vol., i, 414), is now found to be *phenylfluorene peroxide*,  $\text{C}_6\text{H}_4 > \text{CPh} \cdot \text{O} \cdot \text{O} \cdot \text{CPh} < \text{C}_6\text{H}_4$ ; this substance separates from benzene in transparent, tabular crystals containing  $2\text{C}_6\text{H}_6$ , which evolve the solvent on exposure to air and then melt at 193°. This peroxide may also be prepared by shaking a benzene solution of phenyldiphenylenechloromethane with 5 per cent. aqueous sodium peroxide containing some acetic acid. G. T. M.

**Triphenylmethyl. XV.** MOSES GOMBERG and LEE H. CONE (*Ber.*, 1906, 39, 3274—3297. Compare Abstr., 1905, i, 641; Heintschel, Abstr., 1903, i, 243; Jacobson, Abstr., 1905, i, 186).—The present views as to the constitution of triphenylmethyl are (1) that it contains a tervalent carbon atom, (2) that it is hexaphenylethane, and (3) that it is a quinonic substance.

(2) This view can be no longer upheld, as tetraphenyl- and pentaphenylethane have been prepared and found to be stable substances.

(3) Heintschel's formula



does not explain why triphenylmethyl yields triphenylmethyl iodide

when treated with iodine. Jacobson's formula has been discussed previously (Abstr., 1905, i, 641).

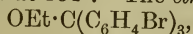
The following halogen substitution products of triphenylmethyl have been prepared by Friedel-Craft's synthesis or by Grignard's reaction (compare Gomberg, Abstr., 1904, i, 489).

*p*-Chlorotriphenylchloromethane, prepared from *p*-chlorobenzophenone and magnesium phenyl bromide, reacts with *p*-toluidine, forming *p*-chlorotriphenylmethyl-*p*-toluidine,  $C_{26}H_{22}NCl$ , melting at  $131^{\circ}$ . The *carbinol*,  $OH \cdot CPh_2 \cdot C_6H_4Cl$ , formed by hydrolysis of the chloride with sulphuric acid, crystallises with difficulty and melts at  $85^{\circ}$ . *p*-Bromotriphenylchloromethane, prepared from *p*-bromobenzophenone and magnesium phenyl bromide, melts at  $114^{\circ}$ . The *carbinol* crystallises slowly and melts at  $74^{\circ}$ . *p*-Iodotriphenylchloromethane, prepared from benzophenone dichloride, iodobenzene, and aluminium chloride, melts at  $123^{\circ}$ .

*Di-p-chlorotriphenylchloromethane*,  $CPhCl(C_6H_4Cl)_2$ , prepared from *p*-chlorobenzophenone and magnesium phenyl bromide and purified by means of its green, iridescent *ferrichloride*,  $C_{19}H_{13}Cl_3 \cdot FeCl_3$ , separates from light petroleum in opaque, crystalline aggregates and melts at  $87^{\circ}$ . The corresponding *di-p-bromo*-compound melts at  $100^{\circ}$ ; the *carbinol* crystallises from light petroleum in opaque masses and melts at  $110^{\circ}$ .

*2:4':4''-Trichlorotriphenylchloromethane*,  $CCl(C_6H_4Cl)_3$ , prepared together with a small quantity of tri-*p*-chlorotriphenylchloromethane, which is more soluble in light petroleum than is the *2:4':4''*-compound, or by the action of carbon tetrachloride and aluminium chloride on chlorobenzene at  $60-70^{\circ}$ , or from magnesium *p*-chlorophenyl iodide and *2:4'*-dichlorobenzophenone, forms large crystals and melts at  $153^{\circ}$ . The corresponding *carbinol*,  $OH \cdot C(C_6H_4Cl)_3$ , crystallises from light petroleum, melts at  $111.5-112.5^{\circ}$ , and on oxidation with chromic acid in glacial acetic acid solution yields *4:4'*-dichlorobenzophenone. *2:4':4''-Trichlorotriphenylmethane*,  $CH(C_6H_4Cl)_3$ , prepared by reduction of the *carbinol* or its chloride with zinc dust and glacial acetic acid, melts at  $106^{\circ}$ . *2:4':4''-Trichlorotriphenylmethyl ethyl ether*,  $OEt \cdot C(C_6H_4Cl)_3$ , prepared by treating the chloride with sodium ethoxide, crystallises slowly and melts at about  $40^{\circ}$ .

*Tri-p-bromotriphenylchloromethane*,  $CCl(C_6H_4Br)_3$ , is the main product of the action of carbon tetrachloride and aluminium chloride on bromobenzene; it crystallises in thin, hexagonal prisms, melts at  $153^{\circ}$ , and gives an orange-red coloration on addition of molecular silver to its solution in benzene. The *carbinol* crystallises in clear, transparent, hexagonal prisms and melts at  $131^{\circ}$ . The *ethyl ether*,



melts at  $206^{\circ}$ .

*2:4':4''-Tribromotriphenylchloromethane*,  $C_{19}H_{12}ClBr_3$ , formed in small amount from carbon tetrachloride and bromobenzene, or by diazotation of pararosaniline, decomposition of the product with cuprous bromide, and treatment with hydrogen chloride in benzene solution, crystallises in small cubes, melts at  $154-155^{\circ}$ , and gives an intense purple colour with molecular silver in benzene solution; the *carbinol* melts at  $134^{\circ}$ ; the *ethyl ether*,  $OEt \cdot C(C_6H_4Br)_3$ , melts at  $5-8^{\circ}$ .



The action of molecular silver and air on the halogen-substituted triphenylchloromethanes in benzene solution leads to the formation of the corresponding peroxides,  $\text{CR}_3 \cdot \text{O} \cdot \text{O} \cdot \text{CR}_3$  (compare Gomberg, *loc. cit.*). The position of the substituting halogen atoms only is given, the temperatures are melting points: *o-monochloro-*,  $150^\circ$ ; *m-monobromo-*,  $170^\circ$ ; *di-p-bromo-*,  $174^\circ$ ; *2:4':4''-trichloro-*,  $140^\circ$ ; *tri-p-chloro-*,  $182^\circ$ ; *tri-p-bromo-*,  $192^\circ$ ; *2:4':4''-tribromo-*,  $153^\circ$ .

These peroxides are obtained also in yields varying from 50—60 to 3—4 per cent. by the action of sodium peroxide on the carbinol chlorides.

Even after some years triphenylmethyl does not lose its power of absorbing oxygen and forming peroxides. In the action of molecular silver and air on the above substituted triphenylchloromethanes, the first product must be the unsaturated substance, the substituted triphenylmethyl, which in the second stage of the reaction absorbs oxygen.

A number of experiments are described to show that if the chloromethane is shaken for a short time with molecular silver and immediately exposed to air, the peroxide is formed, but if the shaking be too prolonged the molecular silver attacks the halogen atoms in the benzene nuclei. The velocity of the reaction varies with the number and nature of the halogens present. Connected with this are (1) the coloration formed when the molecular silver is added to the chloromethane in benzene solution, (2) the amount of halogen removed from the benzene nuclei, and (3) the nature of the resulting product. The results of determinations of (1) and (2) are given in tables. The *product* obtained on prolonged shaking of *2:4':4''-trichlorotriphenylchloromethane* with molecular silver and benzene is an amorphous, light yellow glass which is soluble in benzene or ether. Molecular weight determinations by the cryoscopic method give results which point to the removal of the chlorine being accompanied by the union of two of the triphenylmethyl molecules. This agrees better with Jacobson's than with Heintschel's formula for triphenylmethyl.

The authors conclude that the highly coloured, unstable derivatives of triphenylmethyl must be closely related to the stable triphenylmethane dyes.

G. Y.

**Removal of Chlorine from  $\alpha$ -Chlorinated Fluorene Derivatives.** HERMANN STAUDINGER (*Ber.*, 1906, 39, 3060—3062. Compare Gomberg, this vol., i, 414).—*Phenyldiphenylenemethyl*

[*9-phenylfluoryl*] peroxide,  $\text{C}_6\text{H}_4 > \text{CPh} \cdot \text{O} \cdot \text{O} \cdot \text{CPh} < \text{C}_6\text{H}_4$ , separates after

one to two days, when an ethereal solution of 9-chloro-9-phenylfluorene (obtained conveniently by saturating the carbinol in glacial acetic acid with hydrogen chloride; compare Kliegl, *Abstr.*, 1905, i, 187) is treated with amalgamated zinc in the presence of air and absence of moisture. It separates from benzene in crystals containing  $2\text{C}_6\text{H}_6$  and melts at  $194^\circ$ .

9-Chlorofluorene under similar conditions yields *bisdiphenylene ethane*, which melts at  $239^\circ$ .

Ethyl diphenylenechloroacetate, obtained from phosphoric chloride

and ethyl diphenyleneglycollate, melts at 46—47°, does not react with zinc in ethereal solution, but with molecular silver yields *ethyl bis-diphenylenesuccinate*,  $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{CO}_2\text{Et}) < \begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix}$ , which separates from chloroform or benzene in large crystals and melts at 168—169°.

C. S.

**Dibenzyl-naphthalene.** JOSEF J. VON BOGUSKI (*Ber.*, 1906, 39, 2866—2869).—When naphthalene and benzyl chloride are boiled for some time in the presence of a small quantity of aluminium powder, the products are  $\alpha$ - and  $\beta$ -benzyl-naphthalene and a *dibenzyl-naphthalene*,  $\text{C}_{24}\text{H}_{20}$ . The last compound can be isolated from the fraction boiling at 250—273° under 33 mm. pressure. It forms slender, colourless, triclinic needles, melts at 146·5°, and dissolves in hot alcohol and in most organic solvents.

J. J. S.

**Preparation of a 3:4-Dichloroanilinesulphonic Acid.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 172461).—3:4-Dichloroaniline, when heated with a molecular proportion of sulphuric acid at 215°, yields a sulphonic acid which is probably 3:4-dichloroaniline-6-sulphonic acid. This substance is a white powder, soluble in 200 parts of hot and 1000 parts of cold water, which furnishes a sparingly soluble, colourless diazo-derivative and well-defined sodium salt, crystallising in large, lustrous leaflets. The potassium salt also crystallises readily; the barium, zinc, and copper salts are also soluble.

G. T. M.

**Reduction of Nitro-compounds by Alkaline Solutions of Stannous Oxide.** HEINRICH GOLDSCHMIDT and MORITZ ECKARDT (*Zeit. physikal. Chem.*, 1906, 56, 385—452. Compare Goldschmidt and Ingebrechtsen, *Abstr.*, 1904, ii, 608; Goldschmidt and Sunde, *this vol.*, i, 734).—The relation of the free to the combined alkali in alkaline solutions of stannous hydroxide has been ascertained by determining the solubility of the hydroxide in sodium hydroxide solutions of different strengths. From these determinations it appears that stannous hydroxide acts as a monobasic acid (compare Hantzsch, *Abstr.*, 1902, ii, 395), and that in sodium hydroxide solution it exists chiefly as the salt  $\text{SnO}_2\text{HNa}$ . A saturated solution of stannous hydroxide in pure water is found to contain 0·0000135 gram-mol. per litre, and when this result is combined with the values for the solubility in alkaline solutions, it appears that the affinity constant of stannous hydroxide as an acid is of the same order as that of phenol. The view that stannous hydroxide in sodium hydroxide solutions exists chiefly as the salt  $\text{SnO}_2\text{HNa}$  was confirmed by observing the catalytic effect of these solutions on the change of diacetonealcohol into acetone (see Koelichen, *Abstr.*, 1900, ii, 395). The stannous solutions were prepared by electrolysis of a solution of sodium hydroxide with a tin anode, and the course of the change of the diacetonealcohol into acetone was followed in a dilatometer. Similar experiments indicate that, when alkaline stannous hydroxide solutions are oxidised, the unoxidised product contains sodium and tin in the atomic ratio 2:1.

The character of the reduction by alkaline stannous hydroxide solutions varies very much from one nitro-compound to another. Of the substances studied there are four which react with 3 molecules of stannous hydroxide, and yield amino-compounds directly: these are *o*- and *p*-nitrophenols and *o*- and *p*-nitroanilines. Other substances, namely, *m*-nitrophenol, *m*-nitroaniline, the three nitrobenzoic acids, the three nitrobenzenesulphonic acids, *p*-nitrotoluenesulphonic acid, and *o*-nitrobenzaldehyde, react with 2 molecules of stannous hydroxide. There is, however, further diversity, for whilst of the latter list *o*-nitrobenzoic acid and *o*-nitrobenzaldehyde lead to a hydroxylamine derivative as the end-product of the reaction, the others yield azo- and azoxy-compounds.

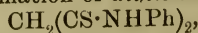
As regards the rate of reduction, the phenomena are simplest when the concentrations of tin and soda are low, and in these cases the velocity coefficient calculated for an equation of the second order is fairly constant. It is probable that the ion  $\text{SnHO}'_2$  is the effective agent in the reduction, and that the nitro-compound is first reduced to a nitroso-compound, which in its turn is further reduced with infinitely great velocity. The value of the velocity coefficient rises markedly as the soda concentration is increased. This increase may be accounted for if it is assumed that in the more concentrated soda solutions disodium stannite is present.

In the following table are compared the values of the velocity coefficient of reduction for various nitro-compounds, (a) with alkaline stannous hydroxide solutions, (b) with stannous chloride and hydrochloric acid:

		Ortho.	Meta.	Para.
Nitroaniline .....	<i>a</i> ...	20	150	13·4
	<i>b</i> ...	0·655	0·175	0·10
Nitrophenol .....	<i>a</i> ...	5·72	40	1·57
	<i>b</i> ...	0·022	0·023	0·0029
Nitrobenzoic acid .....	<i>a</i> ...	97	130	226
	<i>b</i> ...	0·122	0·064	—
Nitrobenzenesulphonic acid	<i>a</i> ...	584	273	484
	<i>b</i> ...	0·052	0·073	0·129
Nitrobenzaldehyde .....	<i>a</i> ...	1030	—	—
	<i>b</i> ...	0·245	0·078	—

J. C. P.

**Sulphur Derivatives of the Anilides of Malonic, Succinic and Phenylacetic Acids and their Transformation Products**  
 ARNOLD REISSERT and ARNOLD MORÉ (*Ber.*, 1906, 39, 3298—3308. Compare Reissert, *Abstr.*, 1904, i, 990).—The action of phosphorus pentasulphide on malonanilide in boiling toluene solution in a reflux apparatus leads to the formation of *dithion-malonanilide*,



which crystallises from alcohol in yellow needles, melts at 149°, and is soluble in aqueous sodium hydroxide, but is insoluble in aqueous sodium carbonate. The *dithion-o-toluidide*,  $\text{CH}_2(\text{CS}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$ , prepared in the same manner from malon-*o*-toluidide, crystallises in yellow



needles and melts at 122—123°. The *dithion-p-toluidide*,  $C_{17}H_{18}N_2S_2$ , melts at 145°.

When shaken with cold concentrated sulphuric acid, dithionmalonanilide yields *dehydrodithionmalonanilide*,  $CH_2<\begin{smallmatrix} C(NPh) \\ C(NPh) \end{smallmatrix}>S_2$ , which crystallises in matted, yellow needles, melts at 154—155°, and is insoluble in aqueous alkali hydroxides.

The action of hot dilute sulphuric acid on dithionmalonanilide leads to the formation of *dehydrodithionmalonanilide sulphide*,  $S[CH<\begin{smallmatrix} C(NPh) \\ C(NPh) \end{smallmatrix}>S_2]_2$ , which crystallises in golden leaflets, melts and decomposes at 197°, and, when boiled with concentrated aqueous sodium hydroxide, yields a small amount of dithionmalonanilide, together with a substance,  $C_{30}H_{22}N_4S_5$ , melting at 210°.

*Thionsuccinanil*,  $\begin{smallmatrix} CH_2 \cdot CO \\ CH_2 \cdot CS \end{smallmatrix} > NPh$ , is formed in only small amount by the action of phosphorus pentasulphide on succinanil, but in good yields by boiling methyl succinanilate with phosphorus pentasulphide in toluene solution. It separates from alcohol in stout, yellow crystals, melts at 116—117°, forms sodium sulphide when heated with aqueous sodium hydroxide, and when treated with cold alcoholic sodium hydroxide yields *sodium thionsuccinanilate*. The free acid,  $NHPh \cdot CS \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , melts at 106—107°.

Methyl succinanilate is prepared best by boiling succinanil with concentrated sulphuric acid and methyl alcohol.

*Benzothiazole-2-propionic acid*,  $C_6H_4<\begin{smallmatrix} S \\ N \end{smallmatrix}>C \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , formed by shaking thionsuccinanilic acid with potassium ferricyanide in alkaline solution, crystallises in stout, white needles, melts at 108—109°, and is soluble in most organic solvents or dilute mineral acids. The *ammonium* and *silver* salts are described; the *methyl ester*,  $C_{11}H_{11}O_2NS$ , crystallises in soft, slender needles and melts at 57—58°; the *anilide*,  $C_7H_4NS \cdot CH_2 \cdot CH_2 \cdot CO \cdot NHPh$ , forms colourless needles and melts at 149°; the *thionanilide*,  $C_7H_4NS \cdot CH_2 \cdot CH_2 \cdot CS \cdot NHPh$ , formed by the action of phosphorus pentasulphide on the anilide in boiling xylene solution, crystallises in stout, yellow needles and melts at 127°.

*s-Dibenzothiazylethane*,  $C_2H_4(C<\begin{smallmatrix} S \\ N \end{smallmatrix}>C_6H_4)_2$  (Hofmann, Abstr., 1880, 388), is formed by oxidation of the preceding substance by means of potassium ferricyanide in alkaline solution.

*Thionphenylacetoanilide*,  $C_{14}H_{13}NS$ , prepared by the action of phosphorus pentasulphide on phenylacetanilide in boiling toluene solution, crystallises in long, soft, silky, yellow needles, melts at 88°, and is readily soluble in aqueous alkali hydroxides.

G. Y.

*Adipanilide*. EYVIND BÖDTKER (Ber., 1906, 39, 2765).—*Adipanilide*,  $C_{18}H_{20}O_2N_2$ , obtained by heating the acid and aniline at 90° for eight hours, crystallises from hot alcohol in glistening plates or feathery needles, melts at 240° (corr.), and dissolves in most organic solvents with the exception of ether.

J. J. S.

*ω*-Sulphonic Acids and *ω*-Cyanides of Aromatic Amines.

HANS BUCHERER and ARTHUR SCHWALBE (*Ber.*, 1906, 39, 2796—2813).

—Sodium methylaniline-*ω*-sulphonate [*anilinomethanesulphonate*],  $\text{NHPh} \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na}$ , is obtained quantitatively by the interaction of formaldehyde bisulphite and aniline and converted into cyanomethylaniline by the action of potassium cyanide; the effect of steam, temperature, acids, and nitrous acid on the yields obtained in this reaction have been investigated. *Sodium monomethyl-p-toluidino-ω-sulphonate*,  $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na}$ , crystallises in large platelets; the sodium salt of the *o*-toluidine derivative gives a flocculent precipitate, and the barium salt crystallises in plates. *Sodium monomethyl-o-anisidine-ω-sulphonate*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na}$ , crystallises in thick, voluminous platelets, the decomposition with potassium cyanide begins at  $90^\circ$ , and the *ω*-cyanomethyl-*o*-anisidine crystallises in glistening prisms melting at  $68^\circ$ . *Sodium monomethyl-p-nitroanilino-ω-sulphonate* separates in yellow needles and does not yield the nitrile.

The disodium salt of dimethyl-*m*-tolylene-2:4-diaminedi-*ω*-sulphonic acid crystallises in needles grouped in stellar aggregates; di-*ω*-cyanodimethyltolylene-2:4-diamine forms faintly yellow-coloured needles melting at  $207^\circ$ . *Sodium monomethyltolylene-2:4-diamine-ω-sulphonate* crystallises in diagonally-crossed needles, the nitrile separates as an oil. *Sodium dimethyl-p-phenylenediaminedi-ω-sulphonate* crystallises in rhombic plates, *ω*-cyanomonomethyl-p-phenylenediamine crystallises in plates melting at  $168^\circ$ ; the sodium salt of the corresponding sulphonate forms minute needles. *Sodium dimethylbenzidinedi-ω-sulphonate* separates in broad needles which are not altered by boiling with water; di-*ω*-cyanodimethylbenzidine melts at  $241$ — $242^\circ$ ; *sodium monomethylbenzidine-ω-sulphonate* separates in bundles of needles, whilst the corresponding *ω*-cyanomonomethylbenzidine crystallises in platelets melting at  $142$ — $144^\circ$  and forms a sparingly soluble diazo-compound which gives rise to red dyes.

*ω*-Cyanomethylanthranilic acid is a light yellow compound melting at  $184^\circ$ . *Sodium methyl-α-naphthylamine-ω-4-disulphonate* crystallises in prisms, *sodium-ω-cyanomethylnaphthionic acid* crystallises in well-formed plates which melt and become brown at  $258^\circ$ . *Sodium methyl-α-naphthylamine-ω-sulphonate* is a colourless, crystalline powder which becomes reddish-violet when exposed to damp air, *ω*-cyanomethyl-*α*-naphthylamine crystallises in long needles melting at  $92^\circ$ , whereas Knoevenagel (*Abstr.*, 1904, i, 989) found  $44$ — $45^\circ$ . The corresponding *ω*-cyanomethyl-*β*-naphthylamine melts at  $102$ — $104^\circ$ .

*Sodium methylethylaniline-ω-sulphonate* crystallises in thick plates and yields 75 per cent. of the nitrile, decomposing with potassium cyanide at  $60^\circ$ . Aniline and benzaldehydebisulphite condense to the sodium benzylaniline-*ω*-sulphonate described by Eibner (*Abstr.*, 1901, i, 376). *ω*-Cyanobenzyl-*o*-anisidine forms minute, glistening prisms melting at  $73^\circ$ .

E. F. A.

Action of Bromine on Dimethylaniline. II. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1906, 36, 409—414. Compare *Abstr.*, 1905, i, 768).—A repetition of the experiments

described in the earlier paper (*loc. cit.*) has shown that a mixture of dimethylaniline, bromine, and chloroform may give two entirely different products even when there is no apparent difference in the conditions of the reaction; thus sometimes the additive compound,  $C_6H_5Br_2 \cdot NMe_2$ , is produced, whilst at other times substitution occurs with formation of the compound  $C_6H_4Br \cdot NMe_2$ ,  $HBr$ ,  $Br$ , described by Fries (*Abstr.*, 1904, i, 571).

E. G.

**A New Method of Preparing Aromatic Amines.** FRANZ SACHS [and in part E. APPENZELLER, VIKTOR HEROLD, B. MYLO, KURT SCHÄDEL, and THEODOR SUTTER] (*Ber.*, 1906, 39, 3006—3028).—In attempting to obtain evidence of the existence of the heteronuclear 2:6-naphthaquinone or its derivatives the author was led to a new method of preparing 5-amino- $\beta$ -naphthol, which consisted in heating sodium  $\beta$ -naphthol-6-sulphonate with sodamide for forty minutes at  $230-240^\circ$  in a copper vessel fitted with a stirrer. In this way the sulphonic residue was eliminated and the  $NH_2$  group introduced into a different position in the ring, and a yield of 51 per cent. of the product was obtained. The process was then extended to other derivatives of the aromatic hydrocarbons.

The sodium salts of benzenesulphonic and naphthalene- $\beta$ -sulphonic acids when fused with sodamide furnished 30 and 32 per cent. of aniline and  $\beta$ -naphthylamine respectively.  $\beta$ -Naphthol-7-sulphonic acid gave rise to a mixture of isomeric aminonaphthols, in which 7-amino- $\beta$ -naphthol and 5-amino- $\beta$ -naphthol were identified.  $\beta$ -Naphthol-8-sulphuric acid also furnished a mixture of isomerides, which were partially separated by means of their benzoyl derivatives.

The basic salt of  $\beta$ -naphthol-1-sulphonic acid yielded a homogeneous product which, however, has not been identified with any of the known aminonaphthols.

$\alpha$ -Naphthol-5-sulphonic acid, when subjected to the sodamide fusion, furnished 5-amino- $\alpha$ -naphthol, which was characterised by the formation of a blue azo-dye with  $\alpha$ -diazonaphthalene-4-sulphonic acid. 8-Amino- $\alpha$ -naphthol itself was not isolated from the sodamide fusion of  $\alpha$ -naphthol-8-sulphonic acid, but was separated from the tarry by-products only in the form of its picrate.

Sodium anthraquinone- $\beta$ -sulphonate, when fused with a mixture of sodamide and naphthalene, yielded anthranol, anthraquinone, and a base melting at  $255^\circ$ , which, although having the composition and molecular complexity of an aminoanthraquinone, is not identical with either  $\alpha$ - or  $\beta$ -aminoanthraquinone.

$\beta$ -Naphthol, when fused with sodamide and excess of naphthalene, yielded principally 6-amino- $\beta$ -naphthol, together with small amounts of 7-amino- $\beta$ -naphthol and the isomeride derived from  $\beta$ -naphthol-1-sulphonic acid; traces of naphthylenediamines were also discernible in the products of fusion.

$\alpha$ -Naphthol gave 5-amino- $\alpha$ -naphthol at  $190^\circ$ , at higher temperatures 1:5-naphthylenediamine results.

$\alpha$ -Naphthylamine, sodamide, and naphthalene, when fused for thirty minutes at  $230^\circ$ , give a 47 per cent. yield of pure 1:5-naphthylenediamine; hydrogenated naphthalenes are produced when the heating is prolonged.



$\beta$ -Naphthylamine under similar conditions gives 2:5-naphthylenediamine and a trace of an ortho-diamine, probably 2:3-naphthylenediamine.

When naphthalene, phenol, and sodamide are fused at 200—220°, amino-groups are introduced into the naphthalene nucleus, and  $\alpha$ -naphthylamine and 1:5-naphthylenediamine are produced, and similar results are obtained when resorcinol or sulphanilic acid are employed in the fusion instead of phenol.

The following substances were employed in characterising the aminonaphthols: dibenzoyl-1-amino- $\beta$ -naphthol, silky needles, melting point 235.5° (compare *Trans.*, 1889, 55, 121); N-benzoyl-3-amino- $\beta$ -naphthol, hexagonal plates, melting point 233.5°; dibenzoyl-4-amino- $\beta$ -naphthol, rhombic plates, melting at 309—310°; dibenzoyl-5-amino- $\beta$ -naphthol, white needles, melting at 223°; N-benzoyl-5-amino- $\beta$ -naphthol, white needles, melting at 152°; diacetyl-5-amino- $\beta$ -naphthol, melting at 187°; acetyl-5-amino-2-methoxynaphthalene, felted needles, melting at 140°; 5-amino- $\beta$ -naphthol picrate, yellow needles, melting point 183°; dibenzoyl-6-amino- $\beta$ -naphthol, prisms, melting at 233.5°; dibenzoyl-7-amino- $\beta$ -naphthol, white needles, melting at 187.5°; dibenzoyl-8-amino- $\beta$ -naphthol, white prisms, melting at 208°; dibenzoyl-4-amino- $\alpha$ -naphthol, rhombic crystals, melting at 215°; dibenzoyl-5-amino- $\alpha$ -naphthol, rhombic plates, melting at 276°.

The following derivatives of 1:8-naphthylenediamine were prepared: dibenzoyl-1:8-naphthylenediamine, needles, melting at 311—312°; ethylidene-1:8-naphthylenediamine, crystallising from dilute alcohol in green needles and decomposing at 210°.

2:6-Dihydroxynaphthalene, when treated with oxidising agents such as ferric chloride, potassium dichromate, ammonium persulphate, manganese dioxide and sulphuric acid, potassium permanganate and potassium hypobromite, furnishes yellowish-white precipitates which dissolve in aqueous alkalis to a green solution; the analytical data and molecular determinations of their oxidation products agree approximately with the formula  $(C_{10}H_6O_2)_4$ .  
G. T. M.

**Substituted Diphenylhydroxylamines.** HEINRICH WIELAND and STEPHAN GAMBARJAN (*Ber.*, 1906, 39, 3036—3042. Compare this vol., i, 453). — *p*-Nitrosodiphenylhydroxylamine,  $NO \cdot C_6H_4 \cdot N(OH) \cdot C_6H_5$ , prepared by Bamberger's method from nitrosobenzene and cold concentrated sulphuric acid, was converted into its methyl ether by shaking with methyl sulphate and dilute aqueous sodium hydroxide; this melted at 137—138° without decomposition; it is soluble in all the organic media. It is markedly basic, and when warmed with moderately concentrated sulphuric acid it undergoes hydrolysis and nitrosobenzene is produced. On reduction either with zinc dust and acetic acid or alcoholic hydrogen sulphide, it yields *p*-aminodiphenylamine.

These reactions are most readily explained on the supposition that *p*-nitrosodiphenylhydroxylamine is a pseudo-acid, which, on the formation of a salt, assumes the quinonoid *aci*-form,  $HO \cdot N : C_6H_4 < \overset{N \cdot C_6H_5}{\underset{O}{\parallel}}$ , and yields a methyl ether having a similar constitution.

2:4-Dinitrodiphenylhydroxylamine,  $C_6H_5 \cdot N(OH) \cdot C_6H_3(NO_2)_2$ , is formed together with dinitrodiphenylamine and aniline when 1-bromo-2:4-dinitrobenzene and phenylhydroxylamine are heated in alcoholic solution in a reflux apparatus. It separates from benzene in flattened, orange-coloured needles melting and decomposing at  $114-115^\circ$ , is readily soluble in most organic media excepting petroleum, and is scarcely soluble in water. In aqueous solutions of ammonia or the alkali hydroxides, it furnishes soluble, brownish-red salts corresponding with the quinonoid *aci*-form. On reduction with zinc dust and acetic acid, diaminodiphenylamine is produced. G. T. M.

Benzoyl-*p*-bromophenylcarbamide: a By-product in the Preparation of Benzoylbromoamide. FORRIS J. MOORE and A. M. CEDERHOLM (*J. Amer. Chem. Soc.*, 1906, 28, 1190—1198).—When benzoylbromoamide is prepared by Hoogewerff and van Dorp's method (Abstr., 1889, 981), it is liable to contain as much as 10 per cent. of benzoyl-*p*-bromophenylcarbamide.

Benzoyl-*p*-bromophenylcarbamide,  $C_6H_4Br \cdot NH \cdot CO \cdot NHBz$ , crystallises in silky needles, melts at  $230^\circ$  in a closed tube, decomposes at  $232^\circ$ , and is soluble in glacial acetic acid and insoluble in water or ether. The compound can be synthesised (1) by the action of phenylcarbamide on benzoylbromoamide in benzene solution, (2) by the action of *p*-bromophenylcarbamide on benzoylbromoamide in alkaline solution, (3) by heating a mixture of *p*-bromophenylcarbamide and benzamide, and (4) by the action of benzoylbromoamide on benzoylphenylcarbamide in benzene solution.

The production of benzoyl-*p*-bromophenylcarbamide in the preparation of benzoylbromoamide is regarded as due to the formation of benzoylphenylcarbamide in the course of the reaction and its subsequent bromination by the benzoylbromoamide itself. E. G.

Action of Bases on Thiocarbamides. REINHOLD VON WALTHER and A. STENZ (*J. pr. Chem.*, 1906, [ii], 74, 222—231. Compare Abstr., 1900, i, 569).—The action of ammonium acetate on *s*-diphenylthiocarbamide in glacial acetic acid solution on the water-bath leads to the formation of hydrogen sulphide and *s*-diphenylcarbamide, but in alcoholic solution to the formation of phenylthiocarbamide.

When heated with hydroxylamine hydrochloride in acetic acid solution, *s*-diphenylthiocarbamide yields *s*-diphenylcarbamide, aniline, and carboxyl sulphide; phenyloxythiocarbamide, formed as an intermediate product in this reaction, yields *s*-diphenylcarbamide, aniline, and carbonyl sulphide when heated with glacial acetic acid.

When heated with hydroxylamine in alcoholic solution, *s*-diphenylthiocarbamide forms sulphur and aniline.

*s*-Diphenylcarbamide, acetanilide, and hydrogen sulphide are formed by heating guanidine with *s*-diphenylthiocarbamide in glacial acetic acid solution (compare Bamberger, Abstr., 1881, 43).

The action of hydrazine on *s*-diphenylthiocarbamide in alcoholic solution on the water-bath leads to the formation of hydrazodicarbonthiophenylamide, together with small amounts of hydrogen sulphide and a substance,  $C_{14}H_{12}N_4S$ , which is obtained also by boiling

2 mols. of *s*-diphenylthiocarbamide with 1 mol. of hydrazine in glacial acetic acid solution; it crystallises in yellow leaflets and melts at 237°.

When boiled with *o*-toluidine in alcoholic solution for one hour, or in glacial acetic acid solution for ten minutes, *s*-diphenylthiocarbamide forms aniline and *ab*-phenyl-*o*-tolylthiocarbamide; *ab*-phenyl-*m*-tolylthiocarbamide is formed in the same manner from *s*-diphenylthiocarbamide and *m*-toluidine.

*ab*-Phenyl-*p*-tolylthiocarbamide melts at 141°; the substance melting at 158° (*loc. cit.*) is a mixture of homologous thiocarbamides (compare Kjellin, Abstr., 1903, i, 287; Hugershoff, *ibid.*, 477). This mixture is formed also by the action of *p*-toluidine on phenylthiocarbimide.

When heated with phenylhydrazine in alcoholic or acetic acid solution, or without a solvent, *s*-diphenylthiocarbamide forms diphenylthiosemicarbazide melting at 177° (Walther, Abstr., 1896, i, 534).

1-Phenyl-4-*p*-tolylthiosemicarbazide formed by heating di-*p*-tolylthiocarbamide, or *ab*-phenyl-*p*-tolylthiocarbamide with phenylhydrazine in glacial acetic acid solution, melts at 165° and remains unchanged when heated with alcoholic hydrogen chloride (compare Marckwald, Abstr., 1893, i, 26; 1899, i, 503).

1-Phenyl-4-*o*-tolylthiosemicarbazide formed from *ab*-phenyl-*o*-tolylthiocarbamide, melts at 156°.

Diphenylmethylthiosemicarbazide is obtained by heating *s*-diphenylthiocarbamide with phenylmethylhydrazine in glacial acetic acid solution; 1:4-diphenylthiosemicarbazide is formed by heating guanylphenylthiocarbamide with an excess of phenylhydrazine. G. Y.

**Behaviour of Carboxylic Acids towards Phenylcarbimide.** WALTER DIECKMANN and FRITZ BREEST (*Ber.*, 1906, 39, 3052—3055).—The action of phenylcarbimide on carboxylic acids leads to the formation of mixed anhydrides,  $\text{RCO}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$ , of phenylcarbamic acid and the corresponding carboxylic acid.

Lævulic acid and phenylcarbimide when mixed in molecular proportions yield a colourless, crystalline mass of the mixed *anhydride*,  $\text{CMeO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$ . This substance, when freshly prepared, is readily soluble in dry ether; it is, however, somewhat unstable and is decomposed into lævulic acid and diphenylcarbamide by water, and by cold alcohol into lævulic acid and ethyl phenylcarbamate. Ammonia resolves it into lævulic acid and diphenylcarbamide. The anhydride evolves carbon dioxide slowly at the ordinary temperature, rapidly at 100°, diphenylcarbamide and lævulic anhydride being produced; some angelicalactone was also noticed. Ethyl lævulate does not interact with phenylcarbimide.

$\beta$ -Benzoylpropionic acid forms a similar mixed anhydride with phenylcarbimide. The additive compound from phenylacetic acid and phenylcarbimide is a colourless, crystalline mass, which is decomposed by water, alcohol, or ammonia. The spontaneous decomposition of this product at the ordinary temperature is complete within forty-eight hours, carbon dioxide is evolved, and the residue consists chiefly of phenylacetanilide together with some diphenylcarbamide and phenylacetic anhydride.



Acetic acid and phenylcarbimide combine with generation of heat to form an additive compound, which is decomposed in about twenty-four hours at the ordinary temperature into carbon dioxide and acetanilide, together with a certain amount of diphenylcarbamide and acetic anhydride.

Dihydrocinnamic acid and phenylcarbimide furnish a crystalline additive compound which slowly evolves carbon dioxide at the ordinary temperature. At  $100^{\circ}$  it decomposes into carbon dioxide, diphenylcarbamide, and dihydrocinnamic anhydride, whilst at  $180^{\circ}$  dihydrocinnamanilide is the chief product. Water, alcohol, and ammonia decompose the mixed anhydride regenerating dihydrocinnamic acid.

The additive products from cinnamic and benzoic acids have similar properties.  
G. T. M.

**Ozonides of Hydro-aromatic Compounds and the Stability of Different Ring Systems.** CARL D. HARRIES and HEINRICH NERESHEIMER (*Ber.*, 1906, **39**, 2846—2850. Compare *Abstr.*, 1904, i, 361, this vol., 261).—*Tetrahydrobenzeneozonide*,  $C_6H_{10}O_3$ , obtained by passing ozone into a chloroform solution of the unsaturated hydrocarbon, forms elastic lumps sparingly soluble in all ordinary solvents. When boiled for some time with water it yields a considerable amount of *n*-adipic acid and a small amount of the corresponding aldehyde.

*m*-Dihydro-xylene (Verley, *Abstr.*, 1898, i, 557) yields a *diozonide*  $C_6H_6Me_2O_6$ , which, after repeated solution in ethyl acetate and precipitation with light petroleum, forms a water-clear syrup with a characteristic odour. It dissolves readily in most organic solvents, is comparatively stable, but occasionally explodes with great violence. When reduced it yields laevulinaldehyde, and hence the hydrocarbon is probably 1:3-dimethyl- $\Delta^{2:6}$ -cyclohexadiene.

The ozonides of hydroaromatic compounds are much more stable than those derived from benzene compounds. Ring systems containing more than six carbon atoms yield ozonides, which are far less stable than those derived from hydroaromatic compounds.  
J. J. S.

**Pseudo-acids.** ARTHUR HANTZSCH (*Ber.*, 1906, **39**, 2703—2705).—A reply to Euler (compare this vol., i, 576).  
C. S.

**Constitution and Colour of Nitrophenols.** ARTHUR HANTZSCH (*Ber.*, 1906, **39**, 3072—3080. Compare this vol., i, 353).—Polemical. A reply to Kauffmann (this vol., i, 577).  
C. S.

**Action of *tert.*-Alkyl Chlorides on *p*-Nitrophenol Salts.** LEOPOLD SPIEGEL and H. KAUFMANN (*Ber.*, 1906, **39**, 2638—2640).—In studying the etherification of *p*-nitrophenol with various alcohols, Spiegel and Sabbath (*Abstr.*, 1901, i, 533) attempted without success to prepare the *tert.*-butyl ether, decomposition taking place at higher temperatures, whilst at lower temperatures the silver salt of *p*-nitrophenol was converted into *p*-nitrophenol by the action of

*tert.*-butyl chloride. The fact, however, that the silver salt in question contains water of crystallisation was overlooked at the time, so that action took place according to the equation  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OAg} + \text{H}_2\text{O} + \text{CMe}_3\text{Cl} = \text{AgCl} + \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + \text{CMe}_3 \cdot \text{OH}$ .

The silver salt is unsuitable for the formation of the tertiary ether, since it does not become anhydrous when heated at  $100^\circ$ , and it decomposes explosively at  $110^\circ$ . The sodium salt, on the other hand, may be dehydrated completely at  $120$ — $130^\circ$ , changing its tint from bright yellow to dark red in the process. When sodium *p*-nitrophenol, *tert.*-butyl chloride, and *tert.*-butyl alcohol are heated at  $110^\circ$  for six hours, sodium chloride and *p*-nitrophenol are obtained. At the same time isobutylene is formed by elimination of hydrogen chloride from the butyl chloride; it was identified by the formation of  $\alpha\beta$ -dibromo- $\beta$ -methylpropane,  $\text{CMe}_2\text{Br} \cdot \text{CH}_2\text{Br}$ , by the action of bromine.

A. McK.

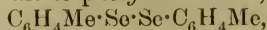
**Solution Equilibrium between 2:4-Dinitrophenol and Aniline.** ROBERT KREMANN (*Monatsh.*, 1906, 27, 627—630. Compare Abstr., 1905, ii, 77; Noelting and Sommerhoff, this vol., i, 157).—The melting-point curve for mixtures of 2:4-dinitrophenol and aniline drops from the melting point of the former and has a break representing a compound melting at  $75^\circ$ .

The influence of the two nitro-groups in the meta-position to each other is greater than that of the nitro- and hydroxy-groups in the ortho-position, as *o*-nitrophenols as such do not form compounds with aniline.

G. Y.

**Selenium Compounds.** F. TABOURY (*Bull. Soc. chim.*, 1906, [iii], 35, 668—674. Compare Abstr., 1903, i, 748).—Selenium reacts readily with magnesium alkyl haloids, and the complexes formed yield on treatment (1) with dilute acids, selenophenols and diselenides; (2) with acid chlorides or anhydrides, esters of the series of acids typified by  $\text{R} \cdot \text{CO} \cdot \text{SeH}$ ; and (3) with alkyl iodides, mixed selenides. The compounds formed are strictly analogous with those obtained by the action of sulphur on magnesium alkyl haloids (Abstr., 1903, i, 748; 1904, i, 493; 1905, i, 56, 644).

Selenophenol boils at  $182^\circ$  (compare Krafft and Lyons, Abstr., 1894, i, 448). Phenyl diselenide melts at  $62^\circ$  (*loc. cit.*).  $\alpha$ -Selenonaphthol,  $\text{C}_{10}\text{H}_7 \cdot \text{SeH}$ , is a slightly yellow liquid, boils at  $165$ — $167^\circ$  under 20 mm. pressure, and evolves hydrogen selenide when heated at atmospheric pressure.  $\alpha$ -Naphthyl diselenide,  $\text{C}_{10}\text{H}_7 \cdot \text{Se} \cdot \text{Se} \cdot \text{C}_{10}\text{H}_7$ , separates from alcohol in orange-yellow prisms and melts at  $87$ — $88^\circ$ . Benzyl  $\alpha$ -naphthyl selenide forms small, colourless prisms, melts at  $68$ — $69^\circ$ , and yields a picrate which separates from ether in orange-red needles and melts at  $118^\circ$ . *p*-Selenocresol,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{SeH}$ , crystallises from ether in colourless lamellae, melts at  $46$ — $47^\circ$ , and rapidly oxidises on exposure to air to *p*-tolyl diselenide,



which separates from alcohol in orange needles and melts at  $47^\circ$ . Benzyl-*p*-tolyl selenide,  $\text{CH}_2\text{Ph} \cdot \text{Se} \cdot \text{C}_6\text{H}_4\text{Me}$ , forms small, unctuous, colourless lamellae and melts at  $32$ — $33^\circ$ . *p*-Tolyl selenobenzoate,

$\text{COPh} \cdot \text{Se} \cdot \text{C}_6\text{H}_4\text{Me}$ , crystallises in colourless prisms, melts at  $71-72^\circ$ , and reddens on exposure to light, due to the liberation of selenium. *p*-Bromoselenophenol separates from ether in colourless lamellæ, melts at about  $75-77^\circ$  and oxidises rapidly on exposure to air, forming *p*-dibromobenzene diselenide,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{Se} \cdot \text{Se} \cdot \text{C}_6\text{H}_4\text{Br}$ , which forms yellow needles from alcohol and melts at  $107-108^\circ$ . *p*-Chloroselenophenol forms small, colourless lamellæ, melts at about  $55^\circ$ , and rapidly oxidises in air to *p*-dichlorobenzene diselenide, yellow needles, melting at  $85-86^\circ$ . *p*-Methoxyphenyl selenobenzoate,  $\text{COPh} \cdot \text{Se} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , forms colourless crystals from alcohol and melts at  $97^\circ$ . *p*-Ethoxyselenophenol is a colourless liquid, heavier than water, boils at  $156-158^\circ$  under 24 mm. pressure, and on oxidation of its solution in dilute potassium hydroxide yields *p*-diethoxyphenyl diselenide,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{Se} \cdot \text{Se} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$ , which crystallises in brilliant yellow lamellæ and melts at  $65^\circ$ . *p*-Ethoxyphenyl selenobenzoate separates from light petroleum in needles and melts at  $94-95^\circ$ .

T. A. H.

**Nitrophenolsulphonic Acids.** ROBERT GNEHM and OSKAR KNECHT (*J. pr. Chem.*, 1906, [ii], 74, 92—111. Compare this vol., i, 578; Franklin, *Abstr.*, 1898, i, 522).—The action of sulphuryl chloride on *o*-nitroanisole leads to the formation of *p*-chloro-*o*-anisole, that of sulphuryl chloride and aluminium chloride to the formation of 4-chloro-2-nitrophenol and 4:6-dichloro-2-nitrophenol, and that of chlorosulphonic acid to the formation of *o*-nitroanisole-*p*-sulphonic acid together with a small amount of *p*-chloro-*o*-nitroanisole.

*o*-Nitroanisole-*p*-sulphonic acid crystallises from water in glistening, transparent plates, or from a mixture of ethyl acetate and benzene in white needles or large, glistening prisms. The ammonium and barium ( $+7\text{H}_2\text{O}$ ) salts are described. *o*-Nitroanisole-*p*-sulphonyl chloride,  $\text{C}_7\text{H}_5\text{O}_5\text{NClS}$ , is prepared by the action of phosphorus pentachloride on ammonium *o*-nitroanisole-*p*-sulphonate on the water-bath, or by the action of nitric acid of sp. gr. 1.475 on anisole-*p*-sulphonyl chloride at  $-7^\circ$  to  $-5^\circ$ ; it crystallises from a mixture of benzene and light petroleum in slender, white needles, melts at  $66^\circ$ , and is hydrolysed on prolonged boiling with water. *o*-Nitroanisole-*p*-sulphonamide,  $\text{C}_7\text{H}_5\text{O}_5\text{N}_2\text{S}$ , prepared by the action of ammonium carbonate on the sulphonyl chloride, crystallises in long, yellowish-white needles and melts at  $146.3^\circ$ .

*Methyl o*-nitroanisole-*p*-sulphonate,  $\text{C}_8\text{H}_9\text{O}_6\text{NS}$ , is obtained in only small amount by the action of an excess of methyl alcohol, whilst sodium *o*-nitroanisole-*p*-sulphonate is formed by the action of sodium methoxide in methyl-alcoholic solution on the sulphonyl chloride. The methyl ester is prepared in good yields by the action of sodium methoxide free from methyl alcohol, on the sulphonyl chloride in benzene solution; it crystallises in glistening, colourless prisms, melts at  $83^\circ$ , and is partially hydrolysed on recrystallisation from water, the unchanged ester separating in thin, white needles.

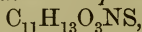
*o*-Anisidine-*p*-sulphonic acid,  $\text{C}_7\text{H}_9\text{O}_4\text{NS}$ , prepared by the reduction of *o*-nitroanisole-*p*-sulphonic acid by means of tin and hydrochloric acid, crystallises in glistening, thin needles, dissolves in water, becoming brown on oxidation by the air, gives a Bordeaux-red color-



tion with ferric chloride, reduces silver nitrate solutions, and forms readily soluble salts; nitrous acid or amyl nitrite converts it into the *diazo*-derivative, which couples with  $\beta$ -naphthol in alkaline solution, forming a bluish-red *azo-dye*. Complete reduction of *o*-nitroanisole-*p*-sulphonyl chloride by means of hydriodic acid, zinc dust and sulphuric acid, or tin and hydrochloric acid leads to the formation of *m*-amino-*p*-methoxythiophenol, which is isolated as the *hydrochloride*,  $C_7H_9ONS \cdot HCl$ ; this crystallises in white, odourless needles, becomes brown at  $170^\circ$ , melts, forming a red liquid, at  $230$ — $235^\circ$ , and is readily soluble in water or aqueous sodium hydroxide. The *mercuric* and *lead* salts are described. The free thiophenol forms stout, yellow, glistening crystals, is unstable, and is rapidly oxidised to the *disulphide hydrochloride*,  $S_2[C_6H_3(OMe) \cdot NH_2]_2$ , which forms white crystals and dissolves slowly in water. The *disulphide* separates from a mixture of toluene and light petroleum in spherical crystals, becomes violet on exposure to air, and gives with concentrated sulphuric acid a light green coloration changing through dark green to dark blue on warming. The action of nitrous acid on *m*-amino-*p*-methoxythiophenol leads to the formation of the *diazo*-derivative of the disulphide; this couples with  $\beta$ -naphthol in alkaline solution, forming a blood-red *azo-dye*,  $S_2[C_6H_3(OMe) \cdot N_2 \cdot C_{10}H_6 \cdot OH]_2$ .

In presence of sodium acetate, the thiophenol hydrochloride condenses with picryl chloride in boiling alcoholic solution, forming the *product*,  $S_2[C_6H_3(OMe) \cdot NH \cdot C_6H_2(NO_2)_3]_2$ , which crystallises in bluish-red, microscopic needles, and when heated melts, forming a red liquid, detonating at higher temperatures.

The *diacetyl* derivative of *m*-amino-*p*-methoxythiophenol,



prepared by heating the hydrochloride with sodium acetate, zinc dust, and acetic anhydride, crystallises in glistening, transparent plates and melts at  $85$ — $86^\circ$ .

Nitration of anisole-*p*-sulphonamide (compare Franklin, *loc. cit.*) leads to the formation of *m*-dinitrobenzene and a syrup which, on treatment with ammonia, yields *o*-nitroanisole-*p*-sulphonamide identical with the product obtained from *o*-nitroanisole.

The oxidation of a mixture of *m*-amino-*p*-methoxythiophenol hydrochloride and dimethyl-*p*-phenylenediaminethiosulphonic acid by means of potassium dichromate in dilute acetic acid solution at  $0^\circ$  leads to the formation of an *indaminethiosulphonic acid*, which forms a reddish-violet solution becoming blue and finally green as the oxidising agent is added, and when boiled with zinc chloride solution is converted into

the *thiazine dye*,  $S_2 \left[ C \begin{array}{c} \diagup \text{CH} \cdot C(NH_2) : C(OMe) \text{---} C \begin{array}{c} \text{C} : N : C : CH : CH \\ \text{C} : S : C : CH : C : NMe_2 \cdot Cl \end{array} \end{array} \right]_2$ .

This is obtained as a dark violet-blue powder with copper lustre, is slightly soluble in hot water, forming a violet-blue solution, gives red to blue flocculent precipitates with dilute hydrochloric or nitric acid, sodium carbonate or hydroxide, or ammonia, is decolorised by stannous chloride in hydrochloric acid solution, and with aqueous sodium sulphide forms a red, flocculent precipitate which is decolorised on heating. It dyes unmordanted cotton wool only feebly, more strongly in presence of sodium sulphide; cotton wool mordanted with tannin

is dyed a pure blue, fast to washing. A table is given showing the results of the spectroscopic examination of the dye. The *acetyl* derivative of the leuco-compound is obtained as an impure yellowish-brown powder melting at 120—121°.

A *résumé* is given of the views of previous authors as to the constitution of the sulphur dyes. G. Y.

**Aminophenolsulphonic and Aminocresolsulphonic Acids.** GUSTAV SCHULTZ (*Ber.*, 1906, 39, 3345—3347).—Aminophenolsulphonic acid III, formed by heating the anilinedisulphonic acid prepared from *m*-aminobenzenesulphonic acid with sodium hydroxide under pressure, is 3-aminophenol-4-sulphonic and not 3-aminophenol-6-sulphonic acid, whilst the anilinedisulphonic acid has the sulphonic groups in the positions 3:6 and not 3:4, as it readily yields benzene-*p*-disulphonic acid when converted into the corresponding hydrazine and boiled with aqueous cupric sulphate.

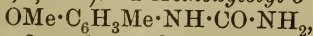
The *anilide*,  $C_6H_4(SO_2 \cdot NHPh)_2$ , crystallises in nacreous leaflets and melts at 249°.

When diazotised and boiled with alcohol, 3-aminophenol-4-sulphonic acid yields an *ethoxyphenolsulphonic acid*. G. Y.

**Preparation of a Di-*o*-anisidinedisulphonic Acid.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 172106).—Benzidine and tolidine on sulphonation furnish complex mixtures of mono- and di-sulphonic acids, sulphones, and sulphonesulphonic acids. It has now been discovered that di-*o*-anisidine, on the contrary, readily yields a homogeneous product consisting of a disulphonic acid when the reaction is effected at low temperatures.

The base is dissolved in four parts of fuming sulphuric acid (10 per cent. of  $SO_3$ ) below 4°; subsequently the solution is heated slowly to 20—25° and then poured on to ice. The *di-*o*-anisidine-6:6'-disulphonic acid*,  $C_{12}H_4(OMe)_2(NH_2)_2(SO_3H)_2$  [3:3':4:4':6:6'], which is somewhat soluble in water, is isolated in the form of its sparingly soluble normal *sodium* salt, this compound separating from its aqueous solution in silvery leaflets containing water of crystallisation. The acid itself is a white, crystalline substance, which may be employed in the production of colouring matters. G. T. M.

**Ethers of Aminocresols and their Derivatives.** LEOPOLD SPIEGEL, N. MUNBLIT, and H. KAUFMANN (*Ber.*, 1906, 39, 3240—3251. Compare Abstr., 1901, i, 533).—2-Methoxytolyl-3-carbamide,



obtained from 3-amino-2-methoxytoluene hydrochloride and carbamide on the water-bath, melts at 150°, and does not have a sweet taste. The corresponding *thiocarbamide*,  $C_9H_{12}ON_2S$ , melts at 137°.

3-Amino-2-ethoxytoluene is a yellow oil; the *hydrochloride*,  $C_9H_{13}ON \cdot HCl$ , melts at 189°, the *carbamide* at 183°, the *thiocarbamide* at 140°.

3-Nitro-2-propoxytoluene, obtained from the potassium salt of the nitrocresol and propyl bromide in propyl alcohol at 160°, is a yellow

oil, which boils at 210—212°. The *amino*-compound is a colourless liquid, the *hydrochloride* of which melts at 178°. The *carbamide*,  $C_{11}H_{16}O_2N_2$ , forms colourless needles and does not have a sweet taste; the *thiocarbamide* melts at 124°.

The *allyl ether* of 3-nitro-2-cresol is a yellow oil; the *amino*-compound is a red oil; the *hydrochloride* melts at 160°. The *carbamide*, obtained from the preceding salt and potassium cyanate, melts at 137°; the *thiocarbamide* at 130°.

The *benzyl ether* of 3-nitro-2-cresol is a red oil. The *amino*-compound, obtained by reduction with iron and 1 per cent. acetic acid solution, forms a *hydrochloride*, which melts at 178°. The *carbamide* melts at 113° and does not have a sweet taste.

*2-Ethoxytolyl-5-carbamide* melts at 158°.

*4-Nitro-2-ethoxytoluene* melts at 61°, the *amino*-compound boils at 249—250°, and the *hydrochloride* melts at 245°. The *carbamide* melts at 161°; the *thiocarbamide* melts at 198° and has a bitter taste.

*2-Ethoxytolyl-4-hydrazine*,  $OEt \cdot C_7H_6 \cdot NH \cdot NH_2$ , obtained by the reduction of the diazotised ethoxytoluidine hydrochloride, is an oil with the odour of phenylhydrazine. The *hydrochloride* melts and decomposes at 185—186°, and in aqueous solution yields, with dextrose and sodium acetate, *2-ethoxytolyl-4-d-glucosazone*,  $C_{24}H_{34}O_6N_4$ , which forms microscopic, yellow crystals and melts at 168°.

*Ethyl 2-ethoxytolyl-4-carbamate*,  $OEt \cdot C_7H_6 \cdot NH \cdot CO_2Et$ , obtained from an ethereal solution of ethyl chlorocarbonate and the ethoxytoluidine, melts at 68°.

The *ethylene ether* of 4-nitro-2-cresol,  $C_2H_4(O \cdot C_7H_6 \cdot NO_2)_2$ , obtained from the potassium salt and ethylene dibromide, forms yellow needles and melts at 202°. The *amino*-compound,  $C_{16}H_{20}O_2N_2$ , melts at 129°; the *carbamide*,  $C_{13}H_{22}O_4N_4$ , melts at 218° and has a faint, bitter taste.

C. S. .

**Constitution of Pseudo-phenols.** KARL AUWERS (*Ber.*, 1906, 39, 3160—3181).—The author had suggested previously a phenolic structure for pseudo-phenols, whereas Zincke sometimes accepts the phenolic structure and sometimes the desmotropic ketonic structure. In the present paper, the author considers the question from the cryoscopic standpoint.

Pseudo-phenols of the type  $CH_2X \cdot C \begin{smallmatrix} \swarrow C(OH):CH \\ \searrow CH-CX' \end{smallmatrix} > CH$ , where X and X' were negative substituents, were studied.

When 5-nitro-2-hydroxybenzyl chloride, melting at 128°, was boiled in acetic acid solution with sodium acetate, 5-nitro-2-hydroxybenzyl acetate,  $OAc \cdot CH_2 \cdot C_6H_3(NO_2) \cdot OH$ , is formed; it separates from benzene in brown crystals and melts at 106.5—108.5°.

5-Nitro-2-hydroxybenzyl bromide,  $CH_2Br \cdot C_6H_3(NO_2) \cdot OH$ , prepared by passing a current of hydrogen bromide into a solution of either of the two preceding compounds at 70—80°, separates from benzene in leaflets and melts at 147°. By the action of bromine it forms 3-bromo-5-nitrobenzyl bromide,  $NO_2 \cdot C_6H_3Br \cdot CH_2Br$ , which separates from glacial acetic acid in needles and melts at 155°. The 6-bromo-derivative of 5-nitro-o-cresol,  $C_7H_6O_3NBr$ , prepared in a similar manner,



separates from glacial acetic acid in needles and melts at 118.5—119.5°.

*Ethyl ω-chloro-6-hydroxy-m-toluate*,  $\text{CH}_2\text{Cl} \cdot \text{C}_6\text{H}_3(\text{CH}_2\text{Cl}) \cdot \text{CO}_2\text{Et}$ , separates from benzene in needles and melts at 119.5°. Its *bromo-*derivative separates from glacial acetic acid in needles and melts at 142—143°.

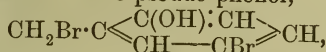
*Ethyl 6-hydroxy-m-toluate*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{Et}$ , prepared by oxidising the corresponding hydroxy-aldehyde by fusion with potash and then esterifying the acid formed, separates from a mixture of benzene and light petroleum in pink needles and melts at 98—99°.

3-Nitro-4-hydroxybenzyl chloride,  $\text{CH}_2\text{Cl} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{OH}$ , melts at 75°, whereas the corresponding bromide,  $\text{C}_7\text{H}_6\text{O}_3\text{NBr}$ , obtained by passing a current of hydrogen bromide into a warm solution of the corresponding alcohol in acetic acid, melts at 83—85° and separates from glacial acetic acid in yellow needles.

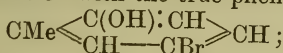
Details of the cryoscopic determinations, which were conducted partly in benzene and partly in *p*-dibromobenzene solutions, are appended.

*m*-Bromo-*o*-hydroxybenzyl bromide behaves towards phenylcarbimide as a hydroxylic substance to form the *urethane*,  $\text{C}_{14}\text{H}_{11}\text{O}_2\text{NBr}_2$ , which crystallises in silky needles and melts at 170—171°.

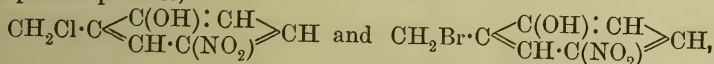
A comparison of the pseudo-phenols and their parent true phenols with regard to cryoscopic behaviour indicates that the pseudo-phenols are phenolic in structure. The pseudo-phenol,



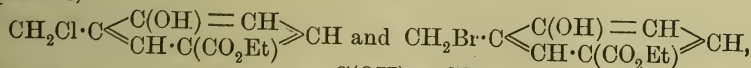
was, for example, contrasted with the true phenol,



the pseudo-phenols,



with the true phenol,  $\text{CMe} \cdot \text{C} \begin{array}{c} \swarrow \text{C(OH):CH} \\ \searrow \text{CH} \cdot \text{C(NO}_2) \end{array} \text{CH}$ ; and the pseudo-phenols,



with the true phenol,  $\text{CMe} \cdot \text{C} \begin{array}{c} \swarrow \text{C(OH)=CH} \\ \searrow \text{CH} \cdot \text{C(CO}_2\text{Et)} \end{array} \text{CH}$ .

The author discusses at length the constitution of pseudo-phenols, and criticises in particular the views of Zincke. A. MCK.

**8-Amino-1-naphthol.** FRITZ FICHTER and RUDOLF GAGEUR (*Ber.*, 1906, 39, 3331—3339. Compare Friedländer and Silberstern, *Abstr.*, 1902, i, 793).—8-Acetylamino-1-naphthol, prepared by treating 8-amino-1-naphthol with finely-powdered sodium acetate, acetic anhydride, and glacial acetic acid, crystallises in colourless, broad needles or plates, melts at 168—169° (138°: Friedländer and Silberstern, *loc. cit.*), and boils at 170—172° under 16 mm. pressure. It reacts with nitrous acid, forming a *nitroso*-derivative,  $\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_2$ , which crystallises in brownish-red needles and decomposes at 175—180°. The *benzoyl*

derivative,  $\text{NHBz} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , crystallises in slender, colourless needles and melts at  $193-194^\circ$ . The *formyl* derivative,  $\text{COH} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , crystallises in reddish-white needles and decomposes at  $140-150^\circ$ .

4-Benzeneazo-8-acetylamino-1-naphthol,  $\text{NPh} \cdot \text{N} \cdot \text{C}_{10}\text{H}_5(\text{NHAc}) \cdot \text{OH}$ , formed by the action of diazobenzene chloride on 8-acetylamino-1-naphthol in alcoholic solution, crystallises in dark red, glistening needles, melts at  $215-216^\circ$ , and on reduction with stannous chloride and hydrochloric acid yields 4:8-diamino-1-naphthol. This forms a *diacetyl* derivative,  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}$ , crystallising in white needles and melting at  $247^\circ$ , and a *triacetyl* derivative,  $\text{OAc} \cdot \text{C}_{10}\text{H}_5(\text{NHAc})_2$ , crystallising in stellate groups of small, white needles and melting at  $258^\circ$ .

The action of bromine on 8-acetylamino-1-naphthol in hot glacial acetic acid solution leads to the formation of *tribromo-2-methylnaphth-peri-oxazole dibromide*,  $\text{C}_{10}\text{H}_3\text{Br}_3 \left\langle \begin{smallmatrix} \text{O} \\ \text{N} \end{smallmatrix} \right\rangle \text{CMe}, \text{Br}_2$ , which crystallises from benzene in shining, yellow, matted, slender needles, melts at  $235^\circ$ , is stable towards alkali hydroxides and acids, and, when reduced with stannous chloride and hydrochloric acid in boiling glacial acetic acid solution, yields *tribromo-2-methylnaphth-peri-oxazole*,  $\text{C}_{11}\text{H}_3\text{OBr}_3\text{Me}$ ; this crystallises in colourless needles, melts at  $215^\circ$ , is insoluble in aqueous alkali hydroxides, and forms the yellow dibromide when treated with bromine in glacial acetic acid solution.

*Tribromo-2-phenylnaphth-peri-oxazole*,  $\text{C}_{10}\text{H}_3\text{Br}_3 \left\langle \begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix} \right\rangle \text{CPh}$ , prepared by the action of bromine on 8-benzoylamino-1-naphthol in hot glacial acetic acid solution, crystallises in slender, glistening needles, melts at  $234^\circ$ , and is highly stable.

8-Acetylamino-1-naphthyl acetate,  $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OAc}$ , formed by boiling 8-amino-1-naphthol hydrochloride with sodium acetate and acetic anhydride, crystallises in white needles, melts at  $118.5^\circ$ , decomposes slightly when distilled under reduced pressure, and when boiled with dilute sodium hydroxide yields 8-acetylamino-1-naphthol. With bromine in glacial acetic acid solution at the ordinary temperature, it forms a *monobromo-derivative*,  $\text{C}_{14}\text{H}_{12}\text{O}_3\text{NBr}$ , melting at  $203^\circ$ , but when boiled with an excess of bromine in glacial acetic acid solution yields *tribromo-2-methylnaphth-peri-oxazole dibromide*.

8-Benzoylamino-1-naphthyl benzoate,  $\text{C}_{24}\text{H}_{17}\text{O}_3\text{N}$ , formed by heating 8-amino-1-naphthol hydrochloride with sodium acetate and an excess of benzoic anhydride, crystallises in large, white needles and melts at  $206-207^\circ$ .

5-Nitro-8-acetylamino-1-naphthyl acetate,  $\text{NO}_2 \cdot \text{C}_{10}\text{H}_5(\text{NHAc}) \cdot \text{OAc}$ , prepared by adding 8-acetylamino-1-naphthyl acetate to an excess of ice-cooled nitric acid of sp. gr. 1.38, crystallises from alcohol in long, light yellow, glistening needles, melts at  $224^\circ$ , and is hydrolysed by boiling dilute sodium hydroxide, yielding 5-nitro-8-acetylamino-1-naphthol,  $\text{NO}_2 \cdot \text{C}_{10}\text{H}_5(\text{NHAc}) \cdot \text{OH}$ ; this crystallises in red needles, melts at  $192^\circ$ , and dissolves in dilute alkali hydroxides, forming a red solution. It couples with diazonium salts in alkaline solution and on reduction with stannous chloride and hydrochloride yields an easily oxidisable diamino-1-naphthol.

8-Acetylamino-1-methoxynaphthalene,  $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OMe}$ , prepared by the action of methyl sulphate on 8-acetylamino-1-naphthol, crystallises in silvery-white needles, melts at  $128^\circ$ , boils at  $138\text{--}140^\circ$  under 14 mm. pressure, and forms a *monobromo-derivative*,  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{NBr}$ , melting at  $124^\circ$ . When boiled with dilute hydrochloric acid, the acetylamino-methyl ether yields the *hydrochloride* of 8-amino-1-methoxynaphthalene,  $\text{C}_{11}\text{H}_{11}\text{ON} \cdot \text{HCl}$ , which crystallises from alcohol; the *picrate*,  $\text{C}_{11}\text{H}_{11}\text{ON} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises in greenish-yellow needles and melts at  $172^\circ$ . The free *base*,  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OMe}$ , is an oil which boils at  $180\text{--}185^\circ$  under 14 mm. pressure, and rapidly darkens. When diazotised and coupled with  $\beta$ -naphthol in sodium carbonate solution, it forms an *azo-compound*,  $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_2$ , which crystallises from benzene in dark violet-red, metallic, hexagonal plates and melts at  $177^\circ$ . When boiled in sulphuric acid solution, the diazonium salt obtained from 8-amino-1-methoxynaphthalene yields the *monomethyl ether* of 1:8-dihydroxynaphthalene; the *picrate*,  $\text{C}_{11}\text{H}_{10}\text{O}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , melts at  $173^\circ$ .

When diazotised in well-cooled dilute solution and boiled with dilute sulphuric acid, 8-amino-1-naphthol yields  $\alpha$ -naphthol. The action of nitrous acid on 8-amino-1-naphthol in concentrated solution leads to the formation of 2-nitroso-8-amino-1-naphthol *hydrochloride*,  $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{NO}) \cdot \text{NH}_2 \cdot \text{HCl}$ , which crystallises in green needles, melts at  $250^\circ$ , and forms a violet coloration with aqueous sodium hydroxide. The concentrated strongly acid solution of the diazonium salt formed together with the nitroso-derivative is reduced by stannous chloride and hydrochloric acid to 2:8-diamino-1-naphthol *hydrochloride*; this crystallises in white needles and forms a *benzylidene* derivative,  $\text{CHPh:N} \cdot \text{C}_{10}\text{H}_5(\text{NH}_2) \cdot \text{OH}$ , which separates from alcohol in yellow needles. The *triacetyl* derivative,  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2$ , forms white, slender needles and melts at  $234^\circ$ .

G. Y.

**Reduction of Aromatic Sulpho-acids to Mercaptans by Alkali Hydrosulphides.** CARL SCHWALBE (*Ber.*, 1906, 39, 3102—3105).—Sodium naphthalene- $\beta$ -sulphonate and a 50 per cent. solution of potassium hydrosulphide are heated for three hours at  $200\text{--}220^\circ$  under a pressure of 10—12 atm. in an iron vessel. The precipitate obtained by heating the product with dilute hydrochloric acid is treated with ether, whereby  $\beta$ -naphthol and the mercaptan are extracted, whilst the disulphide remains undissolved and can be converted into the mercaptan by heating with potassium hydrosulphide and alcohol. The mercaptan yields dyes with diazo-compounds.

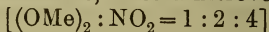
Benzene-sulphonic acid and *m*-disulphonic acid yield coloured products, from which liquids can be obtained having the odour of mercaptans.

Primuline and thioflavin yield dyes containing sulphur. C. S.

**Distribution of Auxochromes in the Molecule.** HUGO KAUFFMANN and W. FRANCK (*Ber.*, 1906, 39, 2722—2726).—The production of colour in a compound containing two or more auxochromes depends not so much on the relative positions of the auxochrome and



chromophore as on the relative positions of the auxochromes themselves. The effect appears to be most pronounced when the two auxochromes are in the para-position, as, for example, in nitroquinol dimethyl ether; the effect is less when they are in the ortho-position, and is practically nil when in the meta-position; thus the ethers of 2- and of 4-nitroresorcinol are nearly colourless. The position of the chromophore is also of influence, since 4-nitroveratrole



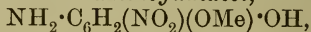
is pale yellow, and the isomeric 3-nitro-compound, colourless. The effect of the positions of the auxochromes is seen by a comparison of 3-nitroveratrole and nitroquinol dimethyl ether.

2-Nitroresorcinol dimethyl ether, obtained by the action of methyl sulphate on 2-nitroresorcinol in the presence of sodium hydrogen carbonate, crystallises from acetic acid in colourless needles, melting at 129—130°.

4-Nitroresorcinol diethyl ether melts at 85°, and the isomeric 2-nitro-compound at 106—107°. J. J. S.

3:4-Diaminoguaiacol. FRITZ FICHTER and JULIUS SCHWAB (*Ber.*, 1906, 39, 3339—3341. Compare Rupe, *Abstr.*, 1898, i, 72).—4-Acetylaminoguaiacyl acetate,  $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}$ , prepared from 4-amino-guaiacol, crystallises from water in silvery scales, melts at 149°, and when boiled with aqueous sodium carbonate yields 4-acetylaminoguaiacol,  $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$ , melting at 118°.

3-Nitro-4-acetylaminoguaiacyl acetate,  $\text{C}_{11}\text{H}_{12}\text{O}_6\text{N}_2$ , prepared by the action of ice-cooled concentrated nitric acid on 4-acetylaminoguaiacyl acetate, crystallises from water or alcohol in yellow, rhombic plates or needles, melts at 158°, and on hydrolysis yields 3-nitro-4-acetylaminoguaiacol,  $\text{C}_8\text{H}_{10}\text{O}_5\text{N}_2$ , crystallising in orange-red prisms and melting at 223°, together with 3-nitro-4-aminoguaiacol,

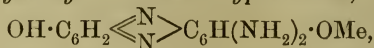


crystallising from benzene or water in light red needles and melting at 169—171°.

3-Nitro-4-benzoylaminoguaiacyl benzoate,  $\text{C}_{21}\text{H}_{16}\text{O}_6\text{N}_2$ , crystallises in yellow, glistening needles and melts at 177°.

Reduction of 3-nitro-4-acetylaminoguaiacyl acetate with stannous chloride and hydrochloric acid leads to the formation of the hydrochloride of 3:4-diaminoguaiacol, which is readily oxidised, and condenses with benzil in alcoholic solution in presence of sodium acetate, forming 7-hydroxy-8-methoxy-2:3-diphenylquinoxaline,  $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_2$ , crystallising in brownish-red, metallic needles and melting at 235°.

2:3-Diamino-8-hydroxy-1:9-dimethoxyphenazine,



is formed by passing a current of air through an aqueous solution of 3:4-diaminoguaiacol hydrochloride in presence of ammonia; it crystallises in glistening scales or almost black, glistening needles, gives with concentrated sulphuric acid a green coloration, becoming blue, violet, and finally red on dilution, dissolves in alcohol, forming a brown solution with green fluorescence, and dyes animal and vegetable fibres a brownish-red.

G. Y.

**Constitution of Guaiacolmonosulphonic Acids and of a Mononitroguaiacol.** LUDWIG PAUL (*Ber.*, 1906, 39, 2773—2782).—*Potassium veratrolesulphonate* crystallises in colourless needles with  $1\frac{1}{2}\text{H}_2\text{O}$  and melts and decomposes at about  $300^\circ$ ; identical preparations are obtained either by sulphonating veratrole or by methylating Heyden's *o*- or *p*-guaiacolsulphonic acids (D.R.-P. 13820). *Veratrolesulphonic chloride* crystallises from ether in needles melting at  $76^\circ$ ; the *amide* forms colourless needles melting at  $136^\circ$ . *5-Nitroguaiacol*, prepared either by the action of fuming nitric acid on acetylguaiacol or by diazotising Cahours' (*Annalen*, 1850, 74, 301) 4-nitro-*o*-anisidine, crystallises in needles and melts at  $104^\circ$ . Its constitution is confirmed by the conversion into Wisinger's  $\beta$ -nitrocatechol methyl ethyl ether (*Abstr.*, 1902, i, 205), and the reduction of this to 4-methoxy-3-ethoxybenzenesulphonic acid, identified by means of its chloride and amides; the latter compound was also obtained from Heyden's *o*-guaiacolsulphonic acid, his *p*-guaiacolsulphonic acid yielding 3-methoxy-4-ethoxybenzenesulphonic acid, of which the *chloride* crystallises in yellow needles and melts at  $72^\circ$ , and the *amide* forms white needles melting at  $192^\circ$ .

E. F. A.

**Behaviour of Cholesterol to Light. II.** ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1906, 48, 546—548. Compare *Abstr.*, 1905, i, 128).—The changes previously described as occurring in cholesterol as the result of the action of light take place similarly in *ischolesterol* from sheep's wool-fat, in *phytosterol* from wheat grains, and in *ergosterol* from the fungus *Boletus edulis*. The changes do not occur in sealed tubes in which the air has been displaced by carbon dioxide, and are therefore probably due to oxidation taking place on exposure to sunlight.

W. D. H.

**Arnidiol Phenylurethane.** TIMOTHÉE KLOBB (*Bull. Soc. chim.*, 1906, [iii], 35, 741—744. Compare *Abstr.*, 1905, i, 594, and Bloch, *Abstr.*, 1904, i, 236).—When heated at  $150$ — $180^\circ$  with ammonia solution in a closed tube, the phenylurethane yields arnidiol, aniline, and carbon dioxide, and when heated alone at  $250$ — $300^\circ$  for two hours in a closed tube it furnishes aniline, carbon dioxide, and a hydrocarbon, *arnidiene*,  $\text{C}_{28}\text{H}_{42}$ . The latter crystallises from ether in needles, melts at  $234$ — $236^\circ$ , and then sublimes. It gives colour reactions similar to those of arnidiol.

T. A. H.

**Preparation of Aminoalkyl Esters.** J. D. RIEDEL (D.R.-P. 169787. Compare this vol., i, 631).—The aminoalkyl esters having the general formula  $\text{NRR}'\cdot\text{CH}_2\cdot\text{CR}''\text{R}'''\cdot\text{O}\cdot\text{X}$ , where R, R', R'', and R''' are aryl or alkyl groups and X is an acyl group, are of great importance therapeutically, because they have the property of producing local anaesthesia without being poisonous; this physiological action seems to depend on the presence in the molecule of a secondary or tertiary amino-group and a tertiary alcohol group, which has been esterified with some suitable aromatic acid.

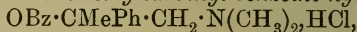
*Dimethylaminotrimethylcarbinyl benzoate hydrochloride,*

$\text{OBz}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{N}(\text{CH}_3)_2\cdot\text{HCl}$ ,

results from the interaction of dimethylaminotrimethylcarbinol and

benzoyl chloride in benzene solution; it crystallises from alcohol in transparent cubes, soluble in water and melting at  $202^{\circ}$ .

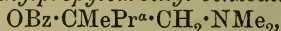
*Phenyl dimethylaminodimethylcarbinyl benzoate hydrochloride,*



obtained from phenyldimethylaminodimethylcarbinol by the Schotten-Baumann reaction, crystallises from alcohol in plates, melts at  $206^{\circ}$ , and is readily soluble in water.

*Dimethylaminodimethylethylcarbinyl benzoate*, an oil boiling at  $149^{\circ}$  under 25 mm. pressure, yields a *hydrochloride* crystallising in needles or leaflets and melting at  $175^{\circ}$  and an *oxalate* which separates in fine needles and melts at  $145^{\circ}$ .

*Dimethylaminodimethylpropylcarbinyl benzoate hydrochloride,*



crystallises from alcohol or ether in small, hygroscopic needles melting at  $146^{\circ}$ .

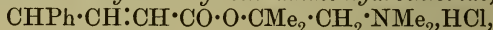
*Dimethylaminodimethylisoamylcarbinyl benzoate hydrochloride,*



crystallises from ether-alcohol in silky needles melting at  $138^{\circ}$ ; it is very soluble in water and insoluble in boiling acetone; its taste is bitter and acrid. The platinichloride melts at  $178^{\circ}$ .

The *hydrochlorides* of dimethylaminomethyldiethylcarbinyl and benzyl-dimethylaminodimethylcarbinyl benzoates are well-defined crystalline salts melting respectively at  $189^{\circ}$  and  $195^{\circ}$ .

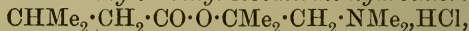
*Dimethylaminotrimethylcarbinyl cinnamate hydrochloride,*



prepared by the interaction of dimethylaminotrimethylcarbinol and cinnamyl chloride in benzene solution, separates in large, tabular crystals which dissolve in acetone and are moderately soluble in hot alcohol, but much less soluble in the cold solvent; it melts at  $208^{\circ}$ .

The cinnamyl derivatives of the other aminoalcohols were similarly prepared, and all yielded well-defined crystalline hydrochlorides with definite melting points.

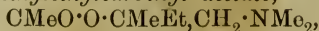
*Dimethylaminotrimethylcarbinyl isovalerate hydrochloride,*



obtained by employing isovaleryl chloride instead of cinnamyl chloride in the preceding preparation, separates in large leaflets which are greasy to the touch and have a bitter taste; it is readily soluble in the ordinary solvents except cold ether and petroleum; it melts indefinitely at  $112^{\circ}$ .

*Dimethylaminodimethylethylcarbinyl diethylcarbamate hydrochloride,*  $\text{NEt}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{CMeEt} \cdot \text{CH}_2 \cdot \text{NMe}_2, \text{HCl}$ , was prepared by heating for one day on the water-bath equivalent quantities of dimethylaminodimethylethylcarbinol and diethylcarbamyl chloride,  $\text{NEt}_2 \cdot \text{COCl}$ ; when recrystallised from ether alcohol it separates in lustrous needles or leaflets and decomposes at  $144^{\circ}$ .

*Dimethylaminodimethylethylcarbinyl acetate,*



was produced by heating the corresponding carbinol with acetic anhydride for four hours at  $120^{\circ}$ ; it boils at  $80-85^{\circ}$  under 32 mm. pressure and rapidly darkens and decomposes on exposure to light.

G. T. M.



Preparation of the Alkali Salts of Organic Acids from the Corresponding Nitriles and Amides. DEUTSCHE GOLD- UND SILBER-SCHNEID-ANSTALT VORM. RÖSSLER (D.R.-P. 169186).—The organic nitriles or amides are hydrolysed by a mixture of equivalent quantities of calcium hydroxide and some alkali salt, such as the carbonate or oxalate, which is capable of forming a sparingly soluble calcium salt, the alkali salt of the organic acid being subsequently obtained by evaporating the filtrate. The process is applicable in the following cases: phenylaminoacetonitrile, acetonitrile, benzonitrile, acetamide, and benzamide.

G. T. M.

Alkylation and Arylation of Anthranilic Acid. JOSEF HOUBEN and WALTER BRASSERT (*Ber.*, 1906, 39, 3233—3240).—Willstätter and Kahn's method (*Abstr.*, 1904, i, 235) for alkylating anthranilic acid was modified by conducting the alkylation with methyl sulphate in glacial acetic acid solution. When a mixture of anthranilic acid, sodium carbonate, water, and methyl sulphate is boiled, methyl methylantranilate is formed in addition to methylantranilic acid.

Whilst a mixture of methylantranilic acid, dimethylantranilic acid, and methyl anthranilate is produced by boiling together anthranilic acid, methyl iodide, and aqueous potassium hydroxide according to H. Meyer's method, it is possible to obtain methylantranilic acid in good yield if an excess of alkali is avoided.

Anthranilic acid may also be methylated by boiling it with methyl sulphate and water. Although in the special case of anthranilic acid the yield of the methylated acid is not as good as that from other methods, the results with *m*- and *p*-aminobenzoic acids are good, and the method is recommended for the methylation of substances which are sensitive towards alkalis.

Anthranilic acid may be ethylated either by H. Meyer's method or by ethyl sulphate. Ethyl bromide is a convenient substitute for ethyl iodide when Meyer's method is used.

Benzylantranilic acid was obtained by boiling together anthranilic acid, water, potassium carbonate, and benzyl chloride. *p*-Nitrobenzylantranilic acid may be prepared in a similar manner.

Phenylantranilic acid was obtained by heating a mixture of anthranilic acid, copper, bromobenzene, sodium carbonate, and water (compare Goldberg, *this vol.*, i, 426).

$\alpha$ -Naphthylantranilic acid was obtained by heating a mixture of anthranilic acid, sodium carbonate, water, copper, and  $\alpha$ -naphthyl bromide.

Allyl chloride differs from propyl and isobutyl chlorides by reacting readily with anthranilic acid and aqueous potassium carbonate to form allylantranilic acid.

A. McK.

Preparation of the Alkamine Esters of *o*- and *m*-Aminobenzoic Acids. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 170587, 172301).—The *o*-nitrobenzoyl ester of diethylaminoethanol is an oil produced by condensing *o*-nitrobenzoyl chloride and diethylaminoethanol in benzene solutions; on reduction it yields an

oily *o*-aminobenzoyl ester, the *monohydrochloride* of which separates from alcohol in colourless crystals and melts at 125—127°.

The *m*-compound can be prepared either in the preceding manner or as follows. Methyl *m*-aminobenzoate was heated for twelve hours with diethylaminoethanol and the excess of the latter removed by distillation under reduced pressure; the product was rendered neutral with hydrochloric acid, in which it dissolved. The solution, after extraction with ether to remove the unaltered methyl *m*-aminobenzoate, was concentrated to obtain *m*-aminobenzoyldiethylaminoethanol hydrochloride, which, when recrystallised from alcohol, separated in colourless prisms melting at 118—120°. The base set free by alkalis solidifies on cooling, and after crystallisation from light petroleum melts at 45—47°.

*m*-Aminobenzoyl- $\alpha$ -hydroxyethylpiperidine was prepared either by heating ethyl *m*-aminobenzoate and  $\alpha$ -hydroxyethylpiperidine or by mixing  $\alpha$ -hydroxyethylpiperidine and *m*-aminobenzoic acid with cold concentrated sulphuric acid and then warming the mixture on the water-bath. In both cases the base was purified by means of its monohydrochloride, then set free by alkalis and recrystallised from light petroleum, when it melted at 73—74°.

*Chloroethyl m*-aminobenzoate, obtained either by esterifying *m*-aminobenzoic acid with ethylene chlorohydrin, or by reducing *m*-nitrobenzoyl ethylene chlorohydrin, was heated with diethylamine at 100—120°. The oily *m*-aminobenzoate of diethylaminoethanol solidified on cooling and was purified by conversion into its monohydrochloride, which crystallised from alcohol in colourless prisms and melted at 118—120°.

The hitherto unknown alkamine esters of the *o*- and *m*-azobenzoic acids are prepared by heating the alkyl azobenzoates with the alkamines; the oily or crystalline products, which are red when reduced with stannous chloride or tin and hydrochloric acid, yield the corresponding alkamine esters of the aminobenzoic acids. Thus *m*-azobenzoylpiperidoethanol, which separates in orange-red crystals melting at 72—74°, furnishes *m*-aminobenzoylpiperidoethanol, melting at 79—80° and yielding a hydrochloride melting at 187—189°.

*o*-Aminobenzoyldiethylaminoethanol is prepared similarly; it is oily and forms a crystalline hydrochloride melting at 125—126°.

*m*-Aminobenzoyldiethylaminoethanol melts at 45—47°; and its hydrochloride at 118—120°. G. T. M.

**Preparation of *N*-Alkylated Alkamine Esters of *o*- and *m*-Aminobenzoic Acids.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172447. Compare preceding abstract).—*N*-Dimethylantranilic acid and diethylaminoethanol when condensed in concentrated sulphuric acid, first at 0° and then on the water-bath, give rise to an oily *alkamine* ester, the hydrochloride of which melts at 135—137°.

*N*-Ethylantranilic acid and hydroxyethylpiperidine, when similarly condensed, yield an oily *alkamine* ester, the hydrated hydrochloride of which melts at 106—108°, whilst the dehydrated substance melts at 142—145°.

The *alkamine* ester, from *m*-dimethylaminobenzoic acid and diethyl-

aminoethanol, is an oil, giving rise to a crystalline hydrochloride melting at  $187^{\circ}$ .  
G. T. M.

**Preparation of the Alkamine Esters of *p*-Aminobenzoic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172568).—The alkamine esters of *p*-aminobenzoic acid may be prepared by heating the alkyl esters of this acid with an alkamine at the boiling point of the latter, the condensation being accompanied by the elimination of alcohol. The *p*-aminobenzoate of *hydroxyethylpiperidine* is obtained in the form of its crystalline *hydrochloride* by heating ethyl *p*-aminobenzoate with *hydroxyethylpiperidine* at  $200$ – $210^{\circ}$  for four to six hours, distilling off the excess of alkamine under reduced pressure, neutralising the residue with dilute hydrochloric acid, filtering off unaltered ethyl *p*-aminobenzoate, and concentrating the filtrate. The alkamine ester itself was set free by alkalis as an oil which soon solidified; after crystallisation from light petroleum, the ester was obtained in colourless needles melting at  $90^{\circ}$ .

The *alkamine* ester from *p*-dimethylaminobenzoic acid and *hydroxyethylpiperidine*, when crystallised from light petroleum, melts at  $38$ – $40^{\circ}$ . The corresponding ester from *hydroxyethyldiethylamine* melted at  $59$ – $60^{\circ}$ . Both these esters form crystallisable hydrochlorides.

The esters may be employed in therapeutics as local anaesthetics.

G. T. M.

**Carbithionic Acids. I. Arylcarbithionic Acids.** JOSEF HOUBEN [with HEINRICH POHL] (*Ber.*, 1906, 39, 3219–3233. Compare Houben and Kesselkaul, *Abstr.*, 1903, i, 42).—*Phenylcarbithionic acid* (*dithiobenzoic acid*),  $C_6H_5 \cdot CS \cdot SH$ , prepared by the action of magnesium phenyl bromide (1 mol.) on carbon disulphide (1 mol.), is a reddish-violet, pungent oil. Its ethereal solution is carmine-red. Its *lead* salt separates from toluene in purple leaflets or needles and melts at  $204.5^{\circ}$  (corr.). Its *zinc* salt is a yellow, amorphous solid and begins to decompose at about  $100^{\circ}$ . Its *mercury* salt separates from benzene in leaflets with a bronze lustre and melts at  $150^{\circ}$ .

*Thiobenzoyl disulphide*,  $S_2(CSPh)_2$ , prepared by the addition of a solution of iodine in potassium iodide to sodium dithiobenzoate, is a crystalline solid and melts at  $92.5^{\circ}$ .

Details are given for the preparation of *benzylcarbithionic acid* (*dithiophenylacetic acid*,  $CH_2Ph \cdot CS_2H$  (compare Houben and Kesselkaul, *loc. cit.*). The *lead* salt separates from benzene in yellow needles and melts at  $149^{\circ}$ . The *zinc* salt crystallises from benzene in yellow leaflets and melts at  $221^{\circ}$ .

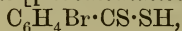
*Thiophenylacetyl disulphide*,  $S_2(CS \cdot CH_2Ph)_2$ , prepared by the action of a solution of iodine in potassium iodide on sodium dithiophenylacetate, melts at  $78^{\circ}$ .

*$\alpha$ -Naphthylcarbithionic acid* ( *$\alpha$ -dithionaphthoic acid*),  $C_{10}H_7 \cdot CS \cdot SH$ , prepared from magnesium  *$\alpha$ -naphthyl* bromide and carbon disulphide, is a dark red oil. Its *lead* salt separates from benzene in needles; its *zinc* salt is a yellow solid; its iron salt,  $(C_{10}H_7 \cdot CS_2)_3Fe$ , separates from ether in green leaflets.



*α-Thionaphthoyl disulphide*,  $S_2(CS \cdot C_{10}H_7)_2$ , prepared by the action of a solution of iodine in potassium iodide on sodium *α*-naphthylcarbithionate, melts at  $169^\circ$ . Its solution in concentrated sulphuric acid assumes a dark blue shade, which disappears on the addition of water. It is oxidised to *α*-naphthoic acid by concentrated nitric acid.

*p*-Bromophenylcarbithionic [*p*-bromodithiobenzoic] acid,



prepared by the action of magnesium *p*-dibromophenyl on carbon disulphide, is a brownish-red oil. Its *lead* salt may be crystallised from benzene or toluene; its *zinc* salt is a yellow, amorphous powder; its *iron* salt is a dark green powder. A. McK.

**Action of Acetyl Bromide on Benzyl Cyanide.** FRANZ KUNCKELL [with F. FLOS] (*Ber.*, 1906, 39, 3145—3146).—*p*-Acetylbenzylcyanide [*p*-acetylphenylacetoneitrile],  $C_6H_4Ac \cdot CH_2 \cdot CN$ , prepared by the addition of aluminium chloride to a mixture of phenylacetoneitrile, acetyl bromide, and carbon disulphide, separates from a mixture of benzene and light petroleum in white needles, melts at  $83-84^\circ$ , and boils with slight decomposition at  $333-334^\circ$ . Its *hydrazone* melts at  $112-114^\circ$ . Its *oxime* separates from benzene in cubes and melts at  $123^\circ$ .

*m*-Acetylphenylacetoneitrile, obtained as a by-product in the preceding reaction, is a yellow oil which boils at  $327-331^\circ$  and has the sp. gr. 1.109 at  $23^\circ$ . When oxidised by permanganate, it yields *isophthalic* acid. A. McK.

**Action of Nascent Hypoiodous Acid on Acids containing an Ethylenic Linking.** Iodo-lactones. J. BOUGAULT (*Compt. rend.*, 1906, 143, 398—400. Compare Abstr., 1905, i, 9).—Acids of the type  $CHR:CH \cdot CH:CH \cdot CO_2H$  (sorbic, piperic, or cinnamylacrylic acid), although containing an ethylenic linking in the  $\gamma\delta$ -position, do not react with iodine and yellow mercuric oxide or iodine and alkali carbonates (nascent hypoiodous acid), but cinnamylisocrotonic acid (this vol., i, 671) yields the iodo-lactone,  $CHPh:CH \cdot CH \begin{smallmatrix} \nearrow CHI \cdot CH_2 \\ \searrow O - CO \end{smallmatrix}$ .

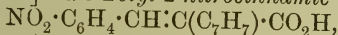
*α*-Ketonic acids of the type  $CHR:CH \cdot CO \cdot CO_2H$  (benzylidene-, piperylidene-, cinnamylidene-, or furfurylidene-pyruvic acid) do not form iodo-lactones by the action of nascent hypoiodous acid, but the corresponding *α*-hydroxy-acids,  $CHR:CH \cdot CH(OH) \cdot CO_2H$ , obtained by the reducing action of sodium amalgam, readily yield iodo-lactones. Neither *β*-benzylidenelaevulinic acid nor cinnamylparaconic acid forms an iodo-lactone, although each contains an ethylenic linking in the  $\beta\gamma$ -position. M. A. W.

**Syntheses and Properties of some New Phenanthrene Derivatives.** ROBERT PSCHORR (*Ber.*, 1906, 39, 3106—3124. Compare Abstr., 1896, i, 303; 1900, i, 232, 233, 487, 488, 489; 1902, i, 96; 1903, i, 167).—[With H. TAPPEN.]—*α*-o-Tolyl-2-nitro-3:4-dimethoxycinnamic acid,  $NO_2 \cdot C_6H_2(OMe)_2 \cdot CH:C(C_7H_7) \cdot CO_2H$ , resulting from the condensation of sodium *o*-tolylacetate (compare Radziszewski and Wispek, Abstr., 1885, 889), *vic*-o-nitrovanillin methyl ether (Abstr., 1899, i, 178), and acetic anhydride at  $100^\circ$ ,

forms slender needles and melts at  $255^{\circ}$  (corr.). The corresponding amino-acid, obtained by reduction with ferrous sulphate and ammonium hydroxide, separates from alcohol in yellow prisms and melts at  $192^{\circ}$  (corr.). The *diazonium chloride*,  $C_{18}H_{18}O_4N_2Cl$ , precipitated from alcoholic solution by ether, forms yellow prisms and melts and decomposes at  $101-102^{\circ}$ .

3:4-Dimethoxy-8-methylphenanthrene-9-carboxylic acid,  $C_{18}H_{16}O_4$ , prepared by warming the diazonium chloride and aqueous sodium carbonate, melts at  $178-180^{\circ}$  (corr.), and by distillation under 160 mm. pressure yields 3:4-dimethoxy-8-methylphenanthrene,  $C_{17}H_{16}O_2$ , which melts at  $68^{\circ}$ .

[With R. HOFMANN.]— $\alpha$ -o-Tolyl-2-nitrocinnamic acid,



obtained from o-nitrobenzaldehyde, acetic anhydride, and sodium o-tolylacetate at  $100^{\circ}$ , melts at  $168^{\circ}$  (corr.), and by reduction yields the amino-acid,  $C_{16}H_{15}O_2N$ , which occurs in two modifications. It separates from alcohol in yellow, hexagonal prisms which melt at  $225^{\circ}$  (corr.), whereas a colourless form is precipitated by acidifying the cold ammoniacal solution of the acid. The latter changes into the yellow modification at  $170^{\circ}$  or in contact with water free from acid.

8-Methylphenanthrene-9-carboxylic acid,  $C_{16}H_{12}O_2$ , is obtained when the diazotised acid in dilute sulphuric acid is treated with copper powder; it crystallises in flat needles, sinters at  $177^{\circ}$ , and melts at  $181-182^{\circ}$  (corr.). By distillation under 160 mm. pressure it yields 1-methylphenanthrene,  $C_{15}H_{12}$ , which melts at  $123^{\circ}$  (corr.) and forms a picrate,  $C_{15}H_{12} \cdot C_6H_3O_7N_3$ , melting at  $139^{\circ}$  (corr.).

1-Methylphenanthrene is quite stable to potassium permanganate, but by potassium dichromate and sulphuric acid is oxidised to 1-methylphenanthraquinone,  $C_{15}H_{10}O_2$ , which forms red leaflets and melts at  $196^{\circ}$  (corr.).

[With F. QUADE.]— $\alpha$ -p-Tolyl-2-nitrocinnamic acid, obtained in a similar manner to the preceding isomeride, melts at  $204^{\circ}$  (corr.). 5-Nitro-8-methylstilbene,  $C_{15}H_{13}O_2N$ , occurring as a by-product, forms red prisms and melts at  $211^{\circ}$  (corr.). The amino-acid,  $C_{16}H_{15}O_2N$ , forms colourless needles, and melts at  $206^{\circ}$  (corr.). After diazotisation, treatment with copper powder in acid solution or warming with aqueous sodium carbonate produces 6-methylphenanthrene-9-carboxylic acid in 20 per cent. yield. A 70 per cent. yield is obtained by diazotising with amyl nitrite in alcoholic hydrogen chloride solution, diluting with water, and adding copper powder. The acid separates from glacial acetic acid in aggregates of light yellow needles, melts at  $238^{\circ}$  (corr.), and by distillation at the ordinary pressure yields 3-methylphenanthrene, which melts at  $65^{\circ}$ , crystallises in long prisms, forms a dibromide melting at  $86-87^{\circ}$ , and a picrate which melts at  $141^{\circ}$  (corr.).

$\alpha$ -p-Tolyl-2-nitro-3:4-dimethoxycinnamic acid,  $C_{18}H_{17}O_6N$ , melts at  $245^{\circ}$  (corr.); the corresponding amino-acid,  $C_{18}H_{19}O_4N$ , at  $203^{\circ}$  (corr.).

3:4-Dimethoxy-6-methylphenanthrene-9-carboxylic acid,  $C_{18}H_{16}O_4$ , forms hexagonal plates, melts at  $253^{\circ}$  (corr.), and by distillation in a vacuum yields 3:4-dimethoxy-6-methylphenanthrene,  $C_{17}H_{16}O_2$ , which

melts at 70—72°, forms a *dibromide*,  $C_{17}H_{16}O_2Br_2$ , melting at 126—127°, and a *picrate*, melting at 118—119°.

[With H. TAPPEN.]—*α-o-Carboxyphenyl-2-nitrocinnamic acid*,

$NO_2 \cdot C_6H_4 \cdot CH : C(C_6H_4 \cdot CO_2H) \cdot CO_2H$ ,  
obtained from sodium homophthalate, melts at 229° (corr.), and by reduction yields the *amino-acid*,  $C_{16}H_{13}O_4N$ , which forms slender needles and melts at 255—256° (corr.).

By warming the solution of the diazotised acid, a mixture of phenanthrene-8 : 9-dicarboxylic acid and its *anhydride* is obtained, which is converted wholly into the latter by crystallisation from glacial acetic acid. It forms glistening needles, melts at 283—284° (corr.), and with ammonia yields the *imide*,  $C_{16}H_9O_2N$ , which sublimes in elongated crystals and melts at 308—309° (corr.). The pure acid has not been obtained.

*α-o-Carboxyphenyl-2-nitro-3 : 4-dimethoxycinnamic acid*,

$NO_2 \cdot C_6H_2(OMe)_2 \cdot CH : C(C_6H_4 \cdot CO_2H) \cdot CO_2H$ ,  
forms yellow needles and melts and decomposes at 259—260° (corr.). The *anhydride*,  $C_{18}H_{13}O_7N$ , also obtained in the condensation, melts at 217° (corr.). The *amino-acid* is obtained readily, but not crystallised, owing to the formation of the *anhydride*. When the diazotised acid is warmed, 3 : 4 dimethoxyphenanthrene-8 : 9-dicarboxylic acid and its *anhydride*,  $C_{18}H_{12}O_5$ , are obtained. By crystallisation, from glacial acetic acid, the mixture is converted entirely into the *anhydride*, which forms yellow needles and melts at 283—284° (corr.).

[With M. SCHÜTZ.]—*α-p-Bromophenyl-2-nitrocinnamic acid*,

$NO_2 \cdot C_6H_4 \cdot CH : C(C_6H_4Br) \cdot CO_2H$ ,  
obtained from sodium *p*-bromophenylacetate (the *amide* of which,  $C_8H_8ONBr$ , melts at 192—194°), crystallises in yellow needles, melts at 187°, and by reduction yields the *amino-acid*,  $C_{15}H_{12}O_2NBr$ , which occurs in yellow needles melting at 213°, or in colourless crystals melting at 222—223°. When the *amino-acid* is warmed with acetic *anhydride* and concentrated sulphuric acid, *β-p-bromophenylcarbostyryl*,  $C_{15}H_{10}ONBr$ , is formed, which melts at 266—267°.

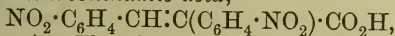
When the acid, dissolved in sodium hydroxide solution, and sodium nitrite, are added to cold dilute sulphuric acid, after some time the diazo-compound separates in yellow flocks. By warming the solution, 3-bromophenanthrene-9-carboxylic acid,  $C_{15}H_9O_2Br$ , is obtained, which forms yellow needles, melts at 290—291°, evolves hydrogen bromide on distillation, and is oxidised to 3-bromophenanthraquinone (compare Schmidt, Abstr., 1904, i, 1034) by chromic and acetic acids.

[With J. POPOVICI.]—*α-o-Bromophenyl-2-nitro-3 : 4-dimethoxycinnamic acid*,  $NO_2 \cdot C_6H_2(OMe)_2 \cdot CH : C(C_6H_4Br) \cdot CO_2H$ , melts at 266—267° (corr.). The *amino-acid*,  $C_{17}H_{16}O_4NBr$ , forms yellow prisms, melts at 218° (corr.), and after diazotisation with amyl nitrite yields 8-bromo-3 : 4-dimethoxyphenanthrene-9-carboxylic acid,  $C_{17}H_{13}O_4Br$ , which separates from hot alcohol in colourless prisms, melts at 228—229° (corr.), and by distillation in a vacuum loses carbon dioxide and hydrogen bromide, yielding a mixture of 8-bromo-3 : 4-dimethoxyphenanthrene, which melts at 81—82°, and the *lactone* of 8-hydroxy-



3:4-dimethoxyphenanthrene-9-carboxylic acid. The former, which is soluble in ether, is purified in the form of the *picrate*, which melts at 117°. The lactone, which is insoluble in ether, separates from alcohol in slender, yellow needles and melts at 160° (corr.). When its solution in sodium hydroxide is acidified, the acid  $C_{17}H_{14}O_5$  is precipitated; it crystallises in long needles and melts at 193° (corr.).

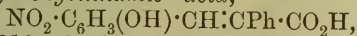
*o*-Nitrophenyl-2-nitrocinnamic acid,



melts at 207° (corr.). The diamino-acid has not been isolated; by acidifying its ammoniacal solution, *o*-aminophenyl-2-aminocinnamic anhydride (3-aminobenzylideneoxindole),  $C_{15}H_{12}ON_2$ , is obtained, which forms yellow prisms and melts at 233—234° (corr.). By treating the diazonium compound with copper powder, the anhydride of 8-aminophenanthrene-9-carboxylic acid,  $C_{15}H_9ON$ , is obtained; it separates from dilute alcohol in faintly yellow prisms and melts at 231° (corr.).

The condensation of *vic*-*o*-aminovanillin and sodium *o*-nitrophenylacetate leads to the formation of the anhydride of *o*-nitrophenyl-2-amino-4-acetoxy-3-methoxycinnamic acid (*o*-nitro-4-acetoxy-3-methoxycarbostryl),  $C_{18}H_{14}O_6N_2$ , which melts at 261° (corr.).

[With F. QUADE.]—The condensation of 2-nitro-5-hydroxybenzaldehyde and sodium phenylacetate leads to the formation of *o*-phenyl-2-nitro-5-hydroxycinnamic acid,



which melts at 219—220°. The amino-acid,  $C_{15}H_{13}O_3N$ , forms yellowish-brown prisms and melts at 237—239° (corr.).

2-Hydroxyphenanthrene-9-carboxylic acid,  $C_{15}H_{10}O_3$ , melts at 278° (corr.), and the acetyl derivative,  $C_{17}H_{12}O_4$ , at 223° (corr.).

*o*-Phenyl-2-nitro-3-acetoxycinnamic acid,  $C_{17}H_{13}O_6N$ , results from the reaction between 2-nitro-3-hydroxybenzaldehyde, sodium phenylacetate, and acetic anhydride; it forms yellow prisms, melts at 254° (corr.), and by reduction and simultaneous hydrolysis yields *o*-phenyl-2-amino-3-hydroxycinnamic acid,  $C_{15}H_{13}O_3N$ , which separates from dilute methyl alcohol in yellow, rhombic plates, melts at 201° (corr.), and does not form phenanthrene derivatives.

C. S.

**Electrolytic Reduction of Aromatic Carboxylic Acids.** CARL METTLER (*Ber.*, 1906, 39, 2933—2942. Compare *Abstr.*, 1905, i, 436; this vol., i, 497).—The reductions were performed in an apparatus consisting of a porous cell, containing a lead anode and filled with dilute sulphuric acid, placed in a beaker containing a lead electrode and the cathode liquid, generally a solution of the acid to be reduced in 20—30 per cent. alcoholic sulphuric acid. A number of aromatic acids were thus reduced to the corresponding alcohols. 3:5-Dichlorosaligenin, obtained from 3:5-dichlorosalicylic acid, crystallised in needles melting at 82°; 3:5-dibromosaligenin melts at 87—88°. The ethyl ether of 3:5-dichloro-*p*-hydroxybenzyl alcohol melts at 86°. *o*-Diphenyldicarboxylic acid is reduced to phenanthraquinone; phthalic acid and terephthalic acid give the corresponding dihydro-derivatives.

E. F. A.

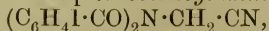
**Preparation of Menthyl Salicylate.** BERTRAND BIBUS and RUDOLF SCHEUBLE (D.R.-P. 171453. Compare Trans., 1903, 83, 1213, and 1904, 85, 1262).—The esterification of menthol is an operation which is effected only with some difficulty owing to the sensitiveness of this alcohol to the action of dehydrating agents, especially when employed at high temperatures. This difficulty is increased when the acid employed also tends to decompose at high temperatures. It has now been found that *menthyl salicylate* may be obtained in fairly good yield (75—80 per cent. of the calculated amount) by heating 30 parts of menthol and 140 parts of salicylic acid at 140—220° in a current of gas such as hydrogen or carbon dioxide. After removing the unchanged acid with aqueous alkali carbonate, the oily residue is fractionated. The ester is a viscid, colourless liquid, having a sweet taste and but very little odour; it is insoluble in water, but dissolves in the ordinary organic solvents. It can only be distilled under diminished pressure, when it boils at 190° and 175° under 15 and 10 mm. pressure respectively. G. T. M.

**Preparation of Tyrosine from Silk.** EMIL ABDERHALDEN and YUTAKA TERUUCHI (*Zeit. physiol. Chem.*, 1906, 48, 528—529).—The usual method of preparing tyrosine from proteids, by hydrolysing with boiling 25 per cent. sulphuric acid and removal of the acid with baryta, is tedious, and leads to loss of tyrosine by its inclusion in the precipitate of barium sulphate. The preparation is simplified by the use of fuming hydrochloric acid, evaporating to dryness, and taking up the residue with water. This is again evaporated to dryness and the procedure repeated. After boiling with animal charcoal, the remaining acid is neutralised exactly with sodium hydroxide, when the tyrosine falls out of solution in an almost pure condition. One recrystallisation renders it quite pure. One kilo. of silk yielded 50—65 grams of tyrosine. Cystine may be obtained in a very similar way. W. D. H.

***o*-, *m*-, and *p*-Iodohippuric Acids.** TREAT B. JOHNSON and HAROLD A. MEADE (*Amer. Chem. J.*, 1906, 36, 294—301).—*o*-Iodohippuric acid,  $C_6H_4I \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$ , obtained by the action of *o*-iodobenzoyl chloride on aminoacetic acid in presence of sodium hydroxide, crystallises from hot water in clusters of radiating needles and melts at 167°. The *nitrile* separates from alcohol in prisms and melts at 158°. The *ethyl* ester forms irregular prisms and melts at 79—80°.

*m*-Iodohippuric acid, prepared by warming an aqueous solution of potassium iodide and *m*-diazohippuric acid, crystallises from hot water in thin plates, melts at 155—156°, and is probably identical with the acid obtained by Griess (Abstr., 1871, 702) by the action of hydriodic acid on diazohippuric acid.

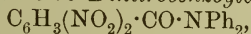
*p*-Iodohippuric acid, obtained by treating aminoacetic acid with *p*-iodobenzoyl chloride, crystallises from hot water in plates and melts at 193°. The *nitrile* separates from alcohol in prismatic crystals and melts at 191—192°. The *ethyl* ester crystallises from alcohol in plates and melts at 128—129°. *Di-p-iodobenzoylaminoacetoneitrile*,



obtained under certain conditions by the action of *p*-iodobenzoyl chloride on aminoacetoneitrile sulphate in presence of sodium hydroxide, crystallises from alcohol in clusters of radiating prisms and melts at 215—216°.

*p*-Iodobenzoylanilide,  $C_6H_4I \cdot CO \cdot NHPh$ , melts at  $210^\circ$ . 3:5-Dinitrobenzoylanilide,  $C_6H_3(NO_2)_2 \cdot CO \cdot NHPh$ , crystallises from alcohol in needles and melts at  $234-235^\circ$ . 3:5-Dinitrobenzoyl-*p*-toluidide,  $C_6H_3(NO_2)_2 \cdot CO \cdot NH \cdot C_6H_4Me$ , does not melt below  $280^\circ$  and is practically insoluble in the usual solvents. 3:5-Dinitrobenzoyl-*o*-toluidide crystallises from alcohol and melts at  $241-242^\circ$ .

[With WALTER C. CHALKER.]—3:5-Dinitrobenzoylmethylanilide,  $C_6H_3(NO_2)_2 \cdot CO \cdot NHPhMe$ , separates from alcohol in prismatic crystals, and melts at  $155-156^\circ$ . 3:5-Dinitrobenzoyldiphenylamide,



crystallises in prisms and melts at  $180-181^\circ$ . 3:5-Dinitrobenzoyl- $\alpha$ -naphthylamide,  $C_6H_3(NO_2)_2 \cdot CO \cdot NH \cdot C_{10}H_7$ , melts at  $268^\circ$  and is insoluble in the ordinary solvents.

E. G.

**Decolorisation of a Faintly Alkaline Solution of Phenolphthalein by Alcohol.** ROBERT COHN (*Zeit. angew. Chem.*, 1906, 19, 1389—1390).—The decolorisation produced by the addition of alcohol to a faintly alkaline solution of phenolphthalein is attributed to the diminution in the dissociation of the colouring matter. The fact that the colour is restored on warming and disappears again on cooling is explained by assuming that the dissociation varies directly with the temperature. The alcohol employed in these experiments was freshly distilled from alkali in order to ensure absence of acid, and it was demonstrated that the colour changes were not brought about by atmospheric carbon dioxide.

P. H.

**Preparation of the Amides of Coumarincarboxylic Acid.** EMANUEL MERCK (D.R.-P. 172724).—Salicylaldehyde and malonamide were heated until the mixture became solid, when the product, after crystallisation from glacial acetic acid, separated in white, felted needles and melted at  $268-269^\circ$ . This substance, coumarincarboxamide, is soluble in methyl and ethyl alcohols and ethyl acetate, but dissolves only sparingly in the other organic solvents.

*Coumarincarboxymethylamide*,  $C_6H_4 \begin{matrix} O-CO \\ | \\ CH:C \cdot CO \cdot NHMe \end{matrix}$ , obtained from salicylaldehyde and *s*-malondimethylamide, crystallises from alcohol in long needles melting at  $172-173^\circ$ ; it is soluble in chloroform, benzene, or toluene.

*Coumarincarboxyanilide*,  $C_6H_4 \begin{matrix} O-CO \\ | \\ CH:C \cdot CO \cdot NHPh \end{matrix}$ , prepared by heating salicylaldehyde and malonanilide, forms long, yellow needles and melts at  $250^\circ$ ; it dissolves readily in the acetone, ethyl acetate, glacial acetic acid, toluene, xylene, and the alcohols, and is only sparingly soluble in benzene, chloroform, light petroleum, or water.

*Coumarincarboxymethylanilide*,  $C_6H_4 \begin{matrix} O-CO \\ | \\ CH:C \cdot CO \cdot NMePh \end{matrix}$ , crystallises from dilute alcohol in aggregates of white needles having a green reflex; it melts at  $139-140^\circ$ .

G. T. M.

**Decomposition of Ethyl Terephthalylldiacetoacetate and a Case of Stereoisomerism.** LUDWIG BEREND and PAUL HERMS (*J. pr. Chem.*, 1906, [ii], 74, 112—141).—Ethyl terephthalylldiacetoacetate,  $C_6H_4(CO \cdot CHAc \cdot CO_2Et)_2$ , prepared by gradually adding



sodium ethoxide in absolute alcoholic solution and terephthalyl chloride in ethereal solution to ethyl acetoacetate, forms a white, fine crystalline powder, sinters at  $90^\circ$ , melts at  $102.5^\circ$ , is readily soluble in chloroform, acetone, benzene, ethyl acetate, or aqueous potassium hydroxide, and gives a red coloration with ferric chloride and a bluish-green precipitate with copper acetate. It is converted by the action of 10 per cent. alcoholic ammonia at  $60^\circ$  into acetamide and *ethyl terephthalaldiacetate*,  $C_6H_4(CO \cdot CH_2 \cdot CO_2Et)_2$ , which crystallises from alcohol in large leaflets, melts at  $70^\circ$ , gives the characteristic colour reaction with ferric chloride, and, when heated with phenylhydrazine in glacial acetic acid solution on the water-bath, yields 3:3'-*p*-phenylenedi-1-phenylpyrazolone,  $C_6H_4(C_3N_2H_2OPh)_2$ ; this melts at  $284^\circ$ , dissolves readily in hot aniline, nitrobenzene, or xylene, is soluble in aqueous sodium hydroxide, gives with copper salts a green, with uranium salts a brownish-red, or with cobalt salts a violet precipitate, and forms an *additive* compound with pyridine, which crystallises in large, white prisms and melts at  $284-285^\circ$ .

On prolonged boiling with water or very dilute sulphuric acid, ethyl terephthalaldiacetoacetate yields ethyl terephthalaldiacetate and benzoylacetone; hydrolysis with 20 per cent. sulphuric acid leads to the formation of diacetylbenzene or, on prolonged boiling, of acetylbenzoic acid, whilst the products of the hydrolysis with 35 per cent. sulphuric acid are acetylbenzoic and terephthalic acids.

Terephthalaldiacetone,  $C_6H_4(CO \cdot CH_2 \cdot COMe)_2$ , is formed synthetically by the action of ethyl terephthalate on acetone in presence of sodamide in absolute ethereal solution; it crystallises in silvery leaflets, assumes a green lustre on repeated recrystallisation, and melts at  $184^\circ$ . It reacts with hydrazine hydrate in hot absolute alcoholic solution, forming *p*-phenylenedi-5-methylpyrazole,  $C_6H_4(C \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{CH} \cdot \text{CMe} \end{smallmatrix})_2$ , which crystallises from alcohol in stellate aggregates of needles, or from glacial acetic acid in leaflets, sinters at  $327^\circ$ , and melts and becomes brown at  $332^\circ$ .

*Ethyl p*-acetylbenzoate,  $COMe \cdot C_6H_4 \cdot CO_2Et$ , prepared by the action of hydrogen chloride on the corresponding nitrile in absolute alcoholic solution, crystallises from water in white needles, melts at  $57^\circ$ , is sparingly soluble in boiling water, has an aromatic odour in aqueous solution, and is only slowly and incompletely volatile in a current of steam.

*p*-Diacetylbenzene is obtained in a 95 per cent. yield by boiling ethyl terephthalaldiacetate with 10 per cent. sulphuric acid; the dioxime melts and decomposes at  $240-245^\circ$  (compare Ingle, Abstr., 1894, i, 589). *p*-Phenylenedi- $\alpha$ -ethyldiamine [*p*-di- $\alpha$ -amino-diethylbenzene]hydrochloride,  $C_6H_4(CHMe \cdot NH_2, HCl)_2$ , is prepared by reduction of the dioxime with sodium amalgam in acid solution and treatment of the base with hydrogen chloride in ethereal solution; it does not melt or decompose in a capillary tube at  $300^\circ$ , but decomposes when heated on platinum, and is readily soluble in water or alcohol. The carbamate,  $C_6H_4 \langle \begin{smallmatrix} CHMe-NH \\ CHMe-NH_3 \end{smallmatrix} \rangle CO_2$ , formed by passing carbon dioxide into the ethereal solution of the base, melts and decomposes at  $85^\circ$ , is soluble

in water, and is decomposed by acids. *i-p*-Di- $\alpha$ -aminodiethylbenzene,  $C_{10}H_{16}N_2$ , is an oil which has a basic odour, distils without decomposition at about  $140^\circ$  under 12 mm. pressure, solidifies to transparent crystals when strongly cooled, and has  $n_D = 1.54126$  at  $21.5^\circ$ . The *d*-tartrate, formed by the action of *d*-tartaric acid on the carbamate, melts and decomposes at  $186^\circ$ , or, after repeated recrystallisations, at  $193$ – $194^\circ$ ; the base obtained from the first fraction has  $[\alpha]_D - 4.55.8'$  at  $22^\circ$ , that from the last fraction  $[\alpha]_D - 5.2.9'$  at  $22^\circ$ . The base obtained from the mother-liquors has  $[\alpha]_D + 18.8.8'$  at  $22^\circ$ .

G. Y.

**Action of Sodium Hypochlorite on Aldoximes.** GIACOMO PONZIO and G. BUSTI (*Atti R. Accad. Sci. Torino*, 1906, 41, 862–868. Compare this vol., i, 482).—Further study of the action of sodium hypochlorite on the aldoximes shows that the latter, besides yielding peroxides of the form  $CHR:N \cdot O \cdot O \cdot N:CHR$ , are partially converted into the corresponding azoximes,  $\begin{array}{c} CR:N \\ | \\ N=CR \end{array} > O$ .

Thus, the interaction of sodium hypochlorite and benzaldoxime gives benzaldoxime peroxide and dibenzenylazoxime (compare Beckmann, *Abstr.*, 1889, 980).

*m*-Nitrobenzaldoxime and sodium hypochloride yield: (1) di-*m*-nitrobenzenylazoxime, which melts at  $169^\circ$ ; Stieglitz (*Abstr.*, 1890, 254) gave the melting point as  $168^\circ$ , Krümmel (*Abstr.*, 1895, i, 661) as  $138^\circ$ , Bamberger and Scheutz (*Abstr.*, 1901, i, 548) as  $147.5$ – $149.5^\circ$  and Franzen and Zimmermann (this vol., i, 388) as  $184^\circ$  (compare also Minunni and Ciusa, this vol., i, 187). (2) *m*-Nitrobenzaldoxime peroxide, melting at  $131^\circ$ ; Minunni and Ciusa (*loc. cit.*) gave the melting point  $105^\circ$ , and Franzen and Zimmermann (*loc. cit.*)  $124^\circ$ .

Anisaldoxime and sodium hypochlorite yield: (1) di-*p*-methoxybenzenylazoxime,  $OMe \cdot C_6H_4 \cdot C \begin{array}{c} \nearrow N \cdot O \\ \searrow N \end{array} \cdot C \cdot C_6H_4 \cdot OMe$ , which crystallises from alcohol or acetic acid in flattened, shining, white needles melting at  $175$ – $176^\circ$  and dissolves readily in chloroform and sparingly in ether. (2) Anisaldoxime peroxide (*p*-methoxybenzaldoxime peroxide), which melts at  $126^\circ$ ; Franzen and Zimmermann (*loc. cit.*) gave the melting point  $119.5^\circ$ .

*Furfuraldoxime peroxide*,  $O_2(N:CH \cdot C_4H_3O)_2$ , prepared by the action of sodium hypochlorite or nitrous acid on furfuraldoxime, crystallises from chloroform in yellow plates which melt and decompose with a slight explosion at  $130^\circ$ .

T. H. P.

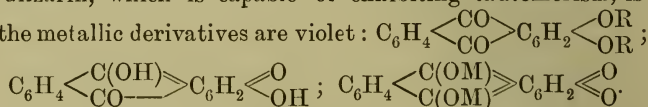
**Piperonal and Hydrogen Chloride: a Two-component Three-phase System.** FORRIS J. MOORE (*J. Amer. Chem. Soc.*, 1906, 28, 1188–1190).—When piperonal is treated with dry hydrogen chloride under a pressure of about one atmosphere, the gas is readily absorbed and a liquid additive compound is produced. On reducing the pressure, hydrogen chloride is rapidly evolved from the liquid and crystals of piperonal separate. A rough measurement has shown that the dissociation pressure is about 500 mm.

A description and diagram are given of an apparatus by means of which these changes can be demonstrated as a lecture experiment in illustration of the phase rule. E. G.

**Relation between Colour and Constitution of Acids, Salts, and Esters.** ARTHUR HANTZSCH (*Ber.*, 1906, 39, 3080—3102).—The term *chromo* is used in preference to *aci*. The prefix *mero* is applied to the names of faintly-coloured hydrogen compounds which consist of solid solutions of the coloured chromo-form in the colourless isomeride. A distinction is drawn between “farbig” and “gefärbt.” The former is applied to substances with specific colour, whilst the latter denotes colourless compounds containing coloured impurities.

Constitutively unchangeable colourless acids produce not only colourless ions, but also colourless ethers, esters, and salts with colourless alkyl or acyl compounds and metals (the oxides of which are colourless) respectively. Constitutively unchangeable coloured acids produce coloured ions, ethers, esters, and salts.

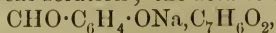
Substances with acidic character are arranged in four classes. (1) Hydrogen, alkyl, acyl, and metallic derivatives are colourless or equally coloured. Such acids are constitutively unchangeable. (2) The hydrogen and alkyl compounds are colourless, whilst the ions and salts exhibit colour. Such substances are pseudo-acids. (3) The hydrogen compound is *coloured*, the alkyl derivatives are colourless, and the ions and salts coloured. In these cases the alkyl compounds are derived from the pseudo-acid, the salts from the real acid, whilst the hydrogen derivative is a mero-compound. (4) This class is complicated and has not been examined thoroughly. Change of colour during salt formation is evidence of intramolecular change. Anthraquinone and its non-isomerisable derivatives, alizarin diacetate and dimethyl ether, are yellow, alizarin, which is capable of exhibiting tautomerism, is red, whilst the metallic derivatives are violet :



[With W. PRÄTORIUS and EDITH MORGAN.]—The alkyl and acyl derivatives of the hydroxybenzaldehydes are colourless. The presence of certain nuclear substituents, especially methoxyl or ethoxyl, may confer colour on the hydroxybenzaldehydes.

The salts and ions of *p*-hydroxybenzaldehyde and of its mono- and dibromo-derivatives are colourless. The salts of the meta-isomeride are colourless when solid or in anhydrous solvents, but form yellow aqueous solutions. The *ammonium* salt,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{ONH}_4$ , is obtained from ammonia and the solid at the ordinary temperature, or in ethereal solution at  $-40^\circ$ .

Salicylaldehyde yields the following colourless salts : the *acid potassium* salt,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{OK}, \text{C}_7\text{H}_6\text{O}_2$ , by the action of potassium ethoxide ( $< \frac{1}{2}$  mol.) on an ethereal solution ; the *acid sodium* salt,



in a similar manner with excess of sodium ethoxide. The *ammonium* salt,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{ONH}_4$ , obtained from ammonia and salicylaldehyde,



dissolves in ether, toluene, or light petroleum, melts at  $85^{\circ}$ . In an atmosphere of ammonia or in alcoholic solution, it changes into hydro-salicylamide. It dissolves in liquid ammonia to an intensely yellow solution of the enolic form,  $\text{CH}(\text{ONH}_4):\text{C}_6\text{H}_4:\text{O}$ , but is recovered colourless after evaporation of the solvent.

Aqueous solutions of these colourless salts are intensely yellow, the colour deepening by warming. The acid sodium salt separates from water or dilute alcohol in yellow leaflets containing  $\frac{1}{2}\text{H}_2\text{O}$ .

The *potassium* salt,  $\text{O}:\text{C}_6\text{H}_4:\text{CH}\cdot\text{OK}$ , is precipitated from aqueous or alcoholic solution by potassium ethoxide (1 mol.). The *lead*, *mercury*, and *thallium* salts are coloured.

Mono- and di-bromosalicylaldehydes are colourless in non-dissociating solvents, and yellow in water or alcohol. The yellow *ammonium* salt,  $\text{O}:\text{C}_6\text{H}_2\text{Br}_2:\text{CH}\cdot\text{ONH}_4$ , obtained from ammonia and dibromosalicylaldehyde, solid or in indifferent solvents, can be crystallised from alcohol or ether; when heated it forms a brominated hydrosalicylamide. The *trimethylamine* and  $\alpha$ -*piperidine* salts are yellow. Resorcinolaldehyde and phloroglucinolaldehyde yield colourless alkali, and yellow lead, thallium, and mercury salts.

The yellow hydrosalicylamide (m. p.  $160^{\circ}$ ) is a chromo-compound,  $\text{N}_2(\text{C}_6\text{H}_4:\text{CH}\cdot\text{OH})_3$ . The colourless isomeride,  $(\text{OH}\cdot\text{C}_6\text{H}_4:\text{CH})_3\text{N}_2$ , resulting from ammonia and the yellow form at  $-40^{\circ}$ , has the same melting point.

[With M. B. BLACKLER.]—The influence of the nature and of the position of substituents on the colour of aromatic hydroxyketones is discussed.

*Potassium p-hydroxybenzophenone*,  $\text{C}_{13}\text{H}_9\text{O}_2\text{K}$ , prepared from potassium ethoxide and an ethereal solution of the ketone, contains 1 mol.  $\text{C}_2\text{H}_6\text{O}$ , which is lost over sulphuric acid. The salt is intensely yellow, as is also the *ammonium* salt.

*3-Bromo-4-hydroxybenzophenone*,  $\text{C}_{13}\text{H}_9\text{O}_2\text{Br}$ , melts at  $180-181^{\circ}$ , forms colourless solutions in indifferent solvents, and yields a yellow *potassium* salt.

*3:5-Dibromo-4-hydroxybenzophenone*,  $\text{C}_{13}\text{H}_8\text{OBr}_2$ , melts at  $151-152^{\circ}$ , is colourless in all solvents, and forms colourless *potassium*, *barium*, *lead*, and *silver* salts.

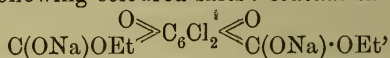
*2:4-Dihydroxyacetophenone* forms colourless solutions in cold alkali hydroxides, which become yellow by warming. The solid *lead*, *silver*, and *mercuric* salts are colourless. *2:4-Dihydroxypropiophenone* has been obtained in colourless crystals containing 1 mol.  $\text{H}_2\text{O}$ , and melting at  $56^{\circ}$ ; the anhydrous substance melts at  $97.5^{\circ}$  and forms colourless salts.

*2-Hydroxy-5-methylbenzophenone* is a merochromo-compound; the solution in light petroleum is colourless, but deposits yellow crystals. The acetyl and benzoyl derivatives, and the same compounds of all coloured aromatic hydroxyketones, are obtained colourless by treating the alkali salt suspended in ether or chloroform with the acid chloride.

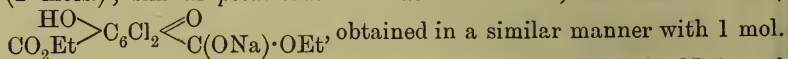
*2:5-Dimethoxybenzophenone* has been obtained colourless. *2:1-Acetylnaphthol* forms yellow solutions, except in light petroleum; the alkali and the barium salts are yellow, whilst the acetyl derivative

which melts at  $107.5^{\circ}$ , and the benzoyl derivative, which melts at  $131^{\circ}$  (compare Ullmann, Abstr., 1897, i, 482), are colourless when prepared as described above. The corresponding ethyl ketone is obtained conveniently by treating a solution of zinc chloride in propionic acid with  $\alpha$ -naphthol at  $160$ — $170^{\circ}$ ; its salts are yellow and the benzoyl derivative colourless. The brominated ketones form yellow needles and melt at  $126$ — $127^{\circ}$  and at  $98^{\circ}$  respectively; their salts are yellow and the acetyl and benzoyl derivatives colourless.

The esters of the hydroxybenzoic acids and their derivatives do not form coloured salts. Selective absorption is first exhibited by the salts of acids containing two pairs of *o*-hydroxy and carbethoxy-groups. Ethyl dichloroquinoldicarboxylate forms colourless salts with tertiary amines ( $\text{HO} > \text{C}_6\text{Cl}_2 < \text{OM}$   
 $\text{CO}_2\text{Et}$  $\text{CO}_2\text{Et}$ ), coloured compounds with secondary amines, and the following coloured salts: *sodium* salt,



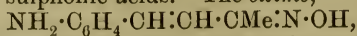
obtained from an alcoholic solution of the ester and sodium ethoxide (2 mols.); similar *potassium* and *rubidium* salts; *acid sodium* salts,



obtained in a similar manner with 1 mol. of sodium ethoxide; the yellow *ammonium* salt,  $\text{C}_{12}\text{H}_{11}\text{O}_6\text{Cl}_2 \cdot \text{NH}_4$ , and the colourless salts with tertiary amines are obtained by the addition of ammonia or of the amine to an ethereal solution of the ester. The ester itself is colourless when solid or in cold alcoholic solution; when fused or in hot alcoholic solution, or in benzene or chloroform, it becomes greenish-yellow and is represented as a merochrome-compound. Similar colour relations are manifested by the salts of quinoldicarboxylic acid and its ethyl ester.

C. S.

**Methineammonium Dyes.** III. HANS RUPE and O. SIEBEL (*Zeit. Farb. Ind.*, 1906, 5, 301—304. Compare Abstr., 1904, i, 107; 1905, i, 83).—*p*-Acetylaminobenzaldehyde,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ , prepared by warming *p*-aminobenzaldehyde with acetic anhydride, crystallises from toluene in yellow needles, melts at  $141^{\circ}$ , and condenses with acetone in presence of sodium hydroxide to form *acetyl-p-aminobenzylidenacetone*,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{COMe}$ ; this crystallises from water in dull yellow needles, melts at  $184^{\circ}$ , and is hydrolysed by sulphuric acid in acetic acid solution, forming *p-aminobenzylidenacetone*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{COMe}$ , which crystallises from 50 per cent. methyl alcohol in yellow leaflets and melts at  $81^{\circ}$ . The base is best prepared by condensing commercial aminobenzaldehyde dissolved in 50 per cent. acetic acid with acetone. On adding dilute hydrochloric acid gradually to a suspension of the base in water, a deep red solution is first produced, which becomes colourless on adding more acid; this behaviour characterises the methineammonium bases. The red solution has strong tinctorial properties. Coloured azo-compounds are formed on coupling diazotised *p*-aminobenzylidenacetone with hydroxy- and amino-naphthalene sulphonic acids. The *oxime*,



of the base, crystallises from alcohol and melts at  $196^{\circ}$ . The *benzoyl*

derivative,  $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{COMe}$ , crystallises from alcohol in yellow needles and melts at  $207^\circ$ . The *thiocarbamide*,

$\text{CS}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{COMe})_2$ , is sparingly soluble in all solvents and melts at  $162^\circ$ . The *hydrazone*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CMe} : \text{N} \cdot \text{NH}_2$ , forms scaly leaflets and melts at  $92^\circ$ .

*p*-Dimethylaminobenzylideneacetone,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{COMe}$ , prepared from dimethylaminobenzaldehyde and acetone at the ordinary temperature, crystallises from alcohol in feebly yellow leaflets and melts at  $132^\circ$ ; the substance described under the same name by Sachs and Lewin (Abstr., 1903, i, 37) is probably a more complex condensation product. The *phenylhydrazone*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CMe} : \text{N} \cdot \text{NHPh}$ , crystallises from alcohol and melts at  $165^\circ$ . The *oxime*,

$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CMe} : \text{N} \cdot \text{OH}$ , crystallises from alcohol in yellow leaflets and melts at  $168^\circ$ . *p*-Dimethylamino-*p*-nitrodibenzylideneacetone,

$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , prepared by the condensation of dimethylaminobenzylideneacetone and *p*-nitrobenzaldehyde, crystallises from glacial acetic acid and melts at  $215^\circ$ ; the *hydrochloride*,  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2 \cdot \text{HCl}$ , is blue, and is decomposed by water. *p*-Dimethylamino-*p*-aminodibenzylideneacetone, obtained by the reduction of the nitro-compound, crystallises from alcohol in intensely red leaflets and melts at  $228^\circ$ .

W. A. D.

Dibenzylideneacetone and Triphenylmethane. I. FRITZ STRAUS and O. ECKER (*Ber.*, 1906, 39, 2977—3006).—*Distyryldichloromethane*,  $\text{CCl}_2(\text{CH} : \text{CHPh})_2$ , prepared by cautiously adding dry phosphorus pentachloride to a boiling solution of dibenzylideneacetone in benzene, forms clusters of silvery leaflets melting at  $77^\circ$ .

*Distyryldichloromethane dichloride*,  $\text{CHPhCl} \cdot \text{CHCl} \cdot \text{CCl}_2 \cdot \text{CH} : \text{CHPh}$ , formed by adding a saturated chloroform solution of chlorine to the keto-chloride dissolved in the same solvent, crystallises from benzene and petroleum in radially-grouped needles melting at  $133^\circ$ . The corresponding *dibromide* crystallises in colourless prisms and melts and decomposes at  $153^\circ$ . *Distyryldichloromethane* when quite dry is not affected by hydrogen chloride, but when dissolved in cold concentrated sulphuric acid it gives a bluish-violet solution with reddish-violet fluorescence; the colour gradually changes to brownish-orange, especially on warming. Hydrogen chloride is evolved, and when the interaction is effected in carbon disulphide solution, the *sulphate*,  $\text{C}_{17}\text{H}_{14}\text{Cl} \cdot \text{SO}_4\text{H} \cdot \text{H}_2\text{SO}_4$ , separates in violet crystals which are extremely sensitive to moisture. When treated with absolute ether, the violet crystals are decomposed, yielding dibenzylideneacetone and an oil containing chlorine. The keto-chloride readily dissolved in liquid sulphur dioxide, and the solution had an appreciable electrical conductivity, although not so great as that of triphenylchloromethane in the same solvent.

*Distyryldichloromethane* combines with metallic chlorides, the *stannichloride*,  $\text{C}_{17}\text{H}_{14}\text{Cl}_2 \cdot \text{SnCl}_4$ , forms violet leaflets with a bronzy lustre, the *mercurichloride* separates in violet-brown needles. Methyl alcohol attacks the keto-chloride, ultimately eliminating both chlorine atoms in the form of hydrogen chloride, and yielding a red, crystalline sub-



stance which could not be purified; glacial acetic acid also removes one chlorine atom, the product being probably the carbinol acetate,  $C(CH:CHPh)_2Cl \cdot OAc$ .

Two *distyrylchlorocarbinol anhydrides*,  $O \begin{matrix} \diagup CCl(CH:CHPh)_2 \\ \diagdown CCl(CH:CHPh)_2 \end{matrix}$ , are produced on shaking an ethereal solution of distyryldichloromethane with water, the total yield being about 40–50 per cent. of the keto-chloride. The mixture, when crystallised from benzene and light petroleum, yields large, hard, transparent prisms decomposing violently at  $147^\circ$ , and slender, soft, light needles decomposing at  $167$ – $169^\circ$ . The substances differ in their behaviour towards warm glacial acetic acid; the prismatic substance furnishes a solid product,  $C_{35}H_{29}OCl$ , melting at  $159$ – $161^\circ$ , whilst the acicular compound yields an oil.

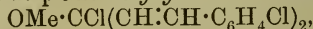
*Di-p-chlorobenzylideneacetone*,  $CO(CH:CH \cdot C_6H_4Cl)_2$ , prepared by condensing *p*-chlorobenzaldehyde and acetone in dilute alcoholic solution in the presence of sodium hydroxide, crystallises in well-defined yellow leaflets and melts at  $193^\circ$ .

*Di-p-chlorostyryldichloromethane*,  $CCl_2(CH:CH \cdot C_6H_4Cl)_2$ , obtained from the preceding compound by the action of phosphorus pentachloride in benzene solution, crystallises from ether in radial aggregates of thick, colourless prisms melting at  $102$ – $103^\circ$ .

The *dibromide*,  $C_6H_4Cl \cdot CHBr \cdot CHBr \cdot CCl_2 \cdot CH:CH \cdot C_6H_4Cl$ , was obtained by treating the keto-chloride with bromine; it crystallises from benzene and petroleum in aggregates of colourless needles melting at  $124$ – $125^\circ$ .

The *stannichloride*,  $C_{17}H_{12}Cl_4 \cdot SnCl_4$ , separates in fine, crystalline aggregates having a metallic lustre.

The *methyl ether of di-p-chlorostyrylchlorocarbinol*,



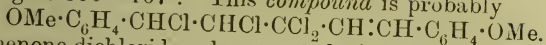
formed by adding a benzene solution of the keto-chloride to a methyl alcohol solution of sodium methoxide, separates from methyl alcohol in aggregates of white needles melting at  $95$ – $96.5^\circ$ . It was not found possible to replace the second chlorine atom by methoxyl, neither could this halogen be removed by reducing agents.

*Di-p-iodobenzylideneacetone*,  $CO(CH:CH \cdot C_6H_4I)_2$ , was prepared by condensing *p*-iodobenzaldehyde and acetone in the presence of alkalis; when crystallised from pyridine, it separated in yellow leaflets melting at  $254$ – $255^\circ$ . This ketone is sparingly soluble in the ordinary organic media.

*Di-p-iodostyryldichloromethane*,  $CCl_2(CH:CH \cdot C_6H_4I)_2$ , crystallises from petroleum in white, crystalline masses or from benzene in white needles melting at  $146$ – $147^\circ$ .

Dianisylideneacetone and phosphorus pentachloride in benzene solution furnish the compound  $CCl_2(CH:CH \cdot C_6H_4 \cdot OMe)_2 \cdot PCl_5 \cdot C_6H_6$ , which separates in green leaflets. When the benzene solution of phosphorus pentachloride and dianisylideneacetone is heated for half an hour, the liquid no longer deposits the green compound on cooling; but on evaporation a grey, crystalline mass is obtained which, after purification, crystallises from carbon disulphide in colourless prisms melting and

decomposing at 106—107°. This compound is probably



Benzophenone dichloride, when treated with methyl alcohol, furnishes dimethoxydiphenylmethane.

The characteristic behaviour of many of these chloro-derivatives with sulphuric acid is described in detail.

G. T. M.

**Ketenes. III. Diphenyleneketene.** HERMANN STAUDINGER (*Ber.*, 1906, 39, 3062—3067. Compare *Abstr.*, 1905, i, 444; this vol., i, 234).—*Chlorodiphenyleneacetyl chloride*,  $\text{C}_6\text{H}_4 > \text{C}(\text{C}_6\text{H}_4) \cdot \text{CCl} \cdot \text{COCl}$ , is

formed in 50 per cent. yield when phosphorus pentachloride reacts with diphenyleneglycollic acid in cold chloroform; it melts at 111·5—112·5°, and reacts with water to regenerate the acid, with alcohol to form ethyl chlorodiphenyleneacetate, which melts at 46—47°, and with aniline to form the *anilide*,  $\text{C}_{20}\text{H}_{14}\text{ONCl}$ , which melts at 177°.

*Diphenyleneketene*,  $\text{C}_6\text{H}_4 > \text{C}(\text{C}_6\text{H}_4) : \text{CO}$ , obtained by the action of zinc on the preceding chloride in ether in the absence of air and moisture, melts at 90—90·5° to a red liquid, decomposes at 150°, and gives an indigo blue coloration with concentrated sulphuric acid. With excess of water it yields diphenyleneacetic acid, whilst the addition of the requisite amount of water to the ketene dissolved in benzene or light petroleum precipitates the *anhydride*,  $\text{C}_{28}\text{H}_{18}\text{O}_3$ , which melts at 164—165°.

Ethyl diphenyleneacetate, prepared from the ketene and ethyl alcohol, or by esterifying the acid, melts at 43—45° and boils at 209—210° under 17 mm. pressure. The *anilide*,  $\text{C}_{20}\text{H}_{15}\text{ON}$ , separates from xylene in slender needles and melts at 255°; the *phenylhydrazide* melts at 234—235°.

From solutions of the ketene in light petroleum, tertiary bases such as quinoline, quinaldine, pyridine, or triethylamine precipitate additive compounds which are decomposed by water; the quinoline compound,  $2\text{C}_{14}\text{H}_8\text{O} \cdot \text{C}_9\text{NH}_7$ , is a white, crystalline powder which darkens at 140° and melts and decomposes at 154—155°. These additive compounds are stable to oxygen, but behave like the ketenes to water, alcohol, aniline, phenylhydrazine, and the Schiff bases. The quinoline compound reacts with water to form a mixture of diphenyleneacetic acid and *quinoline diphenyleneacetate*,  $\text{C}_{14}\text{H}_{10}\text{O}_2 \cdot \text{C}_9\text{NH}_7$ ; the latter melts at 109—110°.

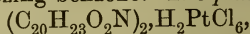
*Bisdiphenyleneallene*,  $\text{C}_6\text{H}_4 > \text{C} : \text{C} : \text{C} < \text{C}_6\text{H}_4$ , forms orange-yellow needles and is obtained by heating the quinoline additive compound with quinoline diphenyleneacetate.

The zinc chloride precipitated in the preparation of diphenyleneketene contains a considerable quantity of the ketene. When the precipitate is oxidised by atmospheric oxygen, fluorenone and a substance,  $\text{C}_{28}\text{H}_{16}\text{O}_3$ , which melts at 269—270° are obtained; the latter is regarded as a tetra-substituted derivative of tetroneic acid,  $\text{C}_6\text{H}_4 > \text{C} \begin{matrix} \text{CO} \cdot \text{O} \\ \text{CO} \end{matrix} \text{C} < \text{C}_6\text{H}_4$ .

C. S.

**Derivatives of Benzoylacetone.** GIOVANNI ISSOGLIO (*Atti R. Accad. Torino*, 1906, 41, 946—960).—When benzoylacetone is treated with acetaldehyde in presence of concentrated ammonia solution, it reacts as if it possessed the enolic structure of  $\beta$ -hydroxy- $\alpha$ -benzoylpropylene,  $\text{OH}\cdot\text{CMe}\cdot\text{CHBz}$ , the following products being obtained.

(1) *Dibenzoyldiisopropylamine*,  $\text{NH}(\text{CHMe}\cdot\text{CH}_2\text{Bz})_2$ , crystallises from benzene in shining, rhombic plates melting at  $127^\circ$ , dissolves in alcohol or chloroform, and to a slight extent in ether, and has the normal molecular weight in freezing benzene. The *platinichloride*,



forms an amorphous precipitate melting at  $198^\circ$ , and the *picrate*,  $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$ , crystallises in microscopic, fern-like aggregates of yellow needles melting and decomposing at  $192^\circ$ .

(2)  *$\beta$ -Ethylidenedibenzoylacetone*,  $\text{CHAcBz}\cdot\text{CHMe}\cdot\text{CBz}\cdot\text{CMe}\cdot\text{OH}$ , crystallises from 60 per cent. alcohol in white needles with a silvery lustre, melts at  $134^\circ$ , and dissolves readily in alcohol, acetone, or chloroform, and less so in benzene.

(3) *3:5-Dibenzoyl-2:4:6-trimethyl-1:4-dihydropyridine (3:5-dibenzoyl-1:4-dihydrocollidine)*,  $\text{CHMe}\langle\begin{smallmatrix} \text{CBz}\cdot\text{CMe} \\ \text{CBz}\cdot\text{CMe} \end{smallmatrix}\rangle\text{NH}$ , crystallises from alcohol in slender, straw-yellow needles, begins to turn brown at  $200^\circ$ , and melts at  $238$ — $239^\circ$ , and is slightly soluble in acetone, chloroform, or benzene. T. H. P.

**The Employment of Vanadium Salts in the Electrolytic Oxidation or Reduction of Organic Compounds.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172654).—Vanadium salts are very suitable depolarisers either at the anode or cathode, and the attack of the oxygen or hydrogen on the organic substance is greatly accelerated.

Finely-pulverised anthracene (4 kilograms) is introduced into a leaden anode cell containing 100 litres of 20 per cent. sulphuric acid with 3 per cent. of vanadic acid. The current density is 300 amperes per square metre with 1.8 volts. After filtering off the anthraquinone, which is rapidly produced in good yield, the electrolytic solution is ready for a further quantity of anthracene.

By the aid of vanadium salts, aniline may be oxidised to benzoquinone, and the latter then reduced to quinol. Azobenzene and azoxybenzene suspended in 20 per cent. sulphuric acid containing two parts of vanadium trioxide are reduced to benzidine in the cathode cell. G. T. M.

**Preparation of Derivatives of the Reduction Products of Anthraquinone.** BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 172930).—The reduction products of anthraquinone, anthranol, hydroxyanthranol and their homologues and sulphonic acids condense with aldehydes to yield substances which are insoluble in alkalis.

Anthranol, when condensed with benzaldehyde in concentrated sulphuric acid at  $30$ — $35^\circ$ , yields a substance which, when crystallised from alcohol, separates in needles melting at  $112$ — $114^\circ$ ; this compound is indifferent towards dilute acids or alkalis, but develops a



magenta coloration with concentrated sulphuric acid. A similar substance can be obtained with hydroxyanthranol.

Anthranol also condenses with para-acetaldehyde: the product is an olive-yellow powder, insoluble in dilute acids or alkalis, but dissolving in concentrated sulphuric acid to a reddish-brown, fluorescent solution.

G. T. M.

**Preparation of the Urethanes of Polynitroaminoanthraquinones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 171588).—It is not possible to introduce into the aminoanthraquinones and their acetyl derivatives more than one nitro-group, and only two of these groups can be introduced into the diaminoanthraquinones and their diacetyl compounds. The urethanes of these amino- and diaminoanthraquinones, on the other hand, can be nitrated readily to furnish polynitro-derivatives which on hydrolysis yield polynitroaminoanthraquinones of great technical importance. The hydrolysis is carried out by heating the nitrated urethane in concentrated sulphuric acid at  $80^{\circ}$  until the evolution of carbon dioxide ceases. In this way, the following compounds were prepared: 2:4-dinitro-1-aminoanthraquinone, 1:3-dinitro-2-aminoanthraquinone, 2:4:6:8-tetranitro-1:5-diaminoanthraquinone, and 2:4:5:7-tetranitro-1:8-diaminoanthraquinone.

These compounds develop characteristic colorations when dissolved in pyridine, concentrated and fuming sulphuric acid, or in a mixture of sulphuric and boric acids.

G. T. M.

**Methylation of Hydroxyanthraquinones.** CARL GRAEBE (*Annalen*, 1906, 349, 201—207. Compare Abstr., 1905, i, 219).—An introduction to the two papers following.

A hydroxy-group in position 1 in anthraquinone is either not methylated or is only very slightly methylated by methyl iodide. A more complete methylation is accomplished by acting on the deoxy-compound, which is afterwards readily oxidised to the anthraquinone ether.

The action of fuming sulphuric acid on alizarin, followed by heating the product with concentrated sulphuric acid, leads to the formation of quinalizarin, hydroxyanthrarufin (which is isolated from the residue by means of boiling toluene, crystallises in red needles, melts at  $270-273^{\circ}$ , and gives a violet coloration with sodium hydroxide or concentrated sulphuric acid) and 1:2:5-trihydroxyanthraquinone-sulphonic acid,  $C_{14}H_8O_8S$ , which is obtained also on prolonged heating of quinalizarin with sulphuric acid; it is obtained as a reddish-yellow precipitate, gives with alkali hydroxides a violet, with acetates a yellowish-red coloration, and yields hydroxyanthrarufin when heated alone or with hydrochloric acid at  $180-200^{\circ}$ .

G. Y.

**Ethers of Alizarin, Flavopurpurin, Hydroxyanthrarufin, and Hydroxychrysazin.** CARL GRAEBE and CARLOS THODE (*Annalen*, 1906, 349, 207—222. Compare preceding abstract, Abstr., 1905, i, 219; Farbenfabriken vorm. Fr. Bayer & Co., Abstr., 1905, i, 362, 532).—*Deoxyalizarin dimethyl ether* (1:2-dimethoxyanthrone),

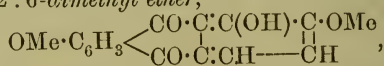
$C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} C_6H_2(OMe)_2$ , prepared by the action of methyl sulphate on deoxyalizarin in 10 per cent. aqueous sodium hydroxide, crystallises in yellow needles, melts at  $150^\circ$ , forms a yellow solution in alcohol or benzene, showing a blue fluorescence when very dilute, and gives a yellow to yellowish-brown coloration with concentrated sulphuric acid. It is insoluble in aqueous sodium hydroxide, is only slowly attacked by boiling alkali hydroxides, remains unchanged when heated with 78 per cent. sulphuric acid at  $100^\circ$ , and does not form an acetyl derivative or an oxime. The *diethyl ether*,  $C_{18}H_{18}O_3$ , crystallises in yellow needles, melts at  $128^\circ$ , gives a yellow to yellowish-brown coloration with concentrated sulphuric acid, and on oxidation yields alizarin diethyl ether.

Alizarin 2-monomethyl ether is formed in small quantity, together with the dimethyl ether, by the action of methyl sulphate on alizarin; it is separated from the dimethyl ether by shaking the benzene solution with aqueous sodium hydroxide. It is obtained also by hydrolysis of the dimethyl ether with sulphuric acid on the water-bath.

Reduction of alizarin dimethyl ether by means of zinc dust and ammonia leads to the formation of deoxyalizarin dimethyl ether, together with an impure *ether*, which is formed also by reduction of deoxyalizarin dimethyl ether, melts at a lower temperature, and on oxidation with chromic acid and glacial acetic acid yields alizarin dimethyl ether.

Alizarin diethyl ether,  $C_{18}H_{16}O_4$ , prepared in a 2 per cent. yield, together with a 5 per cent. yield of the 2-monoethyl ether, by the action of ethyl sulphate on alizarin in aqueous sodium hydroxide solution on the water-bath, crystallises in yellow needles, melts at  $162^\circ$ , and yields the 2-monoethyl ether when heated with 78–80 per cent. sulphuric acid on the water-bath. The descriptions of the diethyl ether given by previous authors are erroneous.

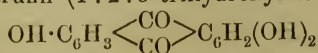
*Flavopurpurin-2:6-dimethyl ether*,



prepared by heating the sodium derivative of flavopurpurin with methyl sulphate at  $160^\circ$ , or by heating the trimethyl ether with sulphuric acid at  $100^\circ$ , crystallises from a mixture of chloroform and carbon disulphide in yellow needles, melts at  $239^\circ$ , forms yellow solutions, is extracted from its solution in benzene or chloroform when shaken with aqueous sodium hydroxide, and forms a red *sodium* derivative and an *acetyl* derivative,  $C_{18}H_{14}O_6$ , which crystallises from glacial acetic acid and melts at  $210^\circ$ .

Deoxyflavopurpurin forms a yellow, crystalline precipitate and melts at  $258^\circ$ ; when heated with methyl sulphate and 10 per cent. sodium hydroxide in an atmosphere of coal gas and oxidised with sodium dichromate and glacial acetic acid, it forms flavopurpurin trimethyl ether, melting at  $225$ – $226^\circ$ , in a 30 per cent. yield.

Hydroxyanthrarufin (1:2:5-trihydroxyanthraquinone),



(compare Graebe, Abstr., 1891, 463), prepared by heating anthrarufin

with sodium nitrate and aqueous sodium hydroxide under pressure at 180—185°, crystallises from glacial acetic acid in yellow or brownish-red needles, melts at 273—274°, forms a violet solution in aqueous alkali hydroxides, gives with concentrated sulphuric acid a violet coloration becoming blue on addition of boric acid, and shows a spectrum with three dark bands of 645—625, 590—570, and 545—530 $\mu$  respectively; it dyes mordanted cotton, colours resembling those obtained with alizarin, but more bluish-red when the mordant is alumina. The *triacetate*,  $C_{20}H_{14}O_8$ , crystallises from alcohol in yellow needles and melts at 229°. The *2-methyl ether* of hydroxyanthrarufin,  $C_{15}H_{10}O_5$ , formed by the action of methyl sulphate and sodium hydroxide on hydroxyanthrarufin, is obtained as a yellow precipitate, melts after recrystallisation from alcohol at 202°, and is not a dye. 1 : 2 : 5-*Trihydroxyanthrone* (*deoxyhydroxyanthrarufin*),  $C_{14}H_{10}O_4$ , prepared by reduction of hydroxyanthrarufin with zinc dust in dilute ammoniacal solution, melts at 258°; when treated with methyl sulphate and 4½ mols. of sodium hydroxide, it yields a *monoethyl ether*,  $C_{15}H_{12}O_4$ , which crystallises from alcohol and melts at 140°.

Hydroxychrysazin (1 : 2 : 8-trihydroxyanthraquinone) crystallises in orange needles, melt at 230° (corr.), forms solutions similar to those of anthrapurpurin, dyes cotton-wool mordanted with alumina brownish-red, or with iron a violet-grey, and gives with sulphuric acid a red coloration becoming violet on addition of boric acid. The *triacetate* melts at 218—219° (compare Liebermann and Giesel, this Journal, 1876, i, 711). On reduction with zinc dust and ammonia on the water-bath, treatment with methyl sulphate and sodium hydroxide, and oxidation with sodium dichromate in boiling glacial acetic acid solution, hydroxychrysazin forms the *trimethyl ether*,  $C_{17}H_{14}O_5$ , which crystallises from methyl alcohol, melts at 157°, and is soluble in benzene or chloroform, but is insoluble in aqueous sodium hydroxide. When heated with sulphuric acid on the water-bath, it is hydrolysed principally to the *dimethyl ether*,  $C_{16}H_{12}O_5$ , forming yellow crystals and melting at 193°, together with small quantities of the *2-monomethyl ether*,  $C_{15}H_{10}O_5$ ; this is prepared by the action of methyl sulphate on hydroxychrysazin in alkaline solution, crystallises in orange-yellow needles, melts at 220°, and is soluble in aqueous sodium hydroxide, but not in the carbonate.

G. Y.

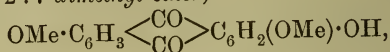
**Methyl Ethers of 2- and 1-Hydroxyanthraquinones, Anthrapurpurin, Purpurin, and Purpuroxanthin.** CARL GRAEBE and HEINRICH BERNHARD (*Annalen*, 1906, 349, 222—231. Compare preceding abstracts).—2-Methoxyanthraquinone, formed by the action of methyl sulphate on 2-hydroxyanthraquinone in alkaline solution, is identical with Kaufler's product from 2-nitroanthraquinone (*Abstr.*, 1904, i, 256).

1-Methoxyanthraquinone is formed only in small quantities by the action of methyl sulphate on erythroxyanthraquinone, but in better yields by the action of methyl sulphate at 100°, or of potassium methyl sulphate at 200°, on the sodium derivative of erythroxyanthraquinone, or by successive reduction of the anthraquinone with zinc dust and glacial acetic acid, methylation, and oxidation; it crystallises from alcohol, melts at 169·5°, and is more stable than alizarin dimethyl



ether towards sulphuric acid, being hydrolysed to 1-hydroxyanthraquinone only very slowly. 1-Methoxyanthrone,  $C_{15}H_{10}O_2$ , melts at  $105^\circ$ .

Anthrapurpurin melts at  $369^\circ$ , the triacetate,  $C_{20}H_{14}O_8$ , melts at  $223-224^\circ$ . The 2:7-dimethyl ether,



prepared by the action of an excess of methyl sulphate and sodium hydroxide on anthrapurpurin, or by the action of 78 per cent. sulphuric acid on anthrapurpurin trimethyl ether on the water-bath, crystallises from benzene, melts at  $241^\circ$ , and forms a red sodium derivative.

The trimethyl ether of anthrapurpurin,  $C_{17}H_{14}O_5$ , prepared by methylation and oxidation of deoxyanthrapurpurin, crystallises from alcohol in yellow needles, melts at  $201^\circ$ , and is readily soluble in benzene, chloroform, or hot alcohol.

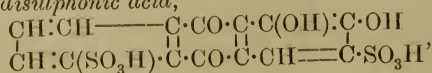
The action of an excess of sodium hydroxide and methyl sulphate on purpurin leads to the formation of the 2-monomethyl ether. The 3-methyl ether of purpuroxanthin,  $C_{15}H_{10}O_4$ , formed by the action of methyl sulphate and sodium hydroxide on purpuroxanthin, crystallises from benzene and melts at  $193^\circ$ ; the benzene mother liquors contain a dimethyl ether crystallising in yellow needles and melting at  $150-153^\circ$  (compare Boeck, Abstr., 1905, i, 531). G. Y.

**Conversion of Aromatic Ketones into the Corresponding Imides.** MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1906, [iii], 35, 666-668. Compare this vol., i, 193).—Hydroxyanthraquinones may be readily converted into the corresponding imides by heating them in glycerol with a normal ammonium salt of an organic acid or with ammonium carbonate. Under similar conditions, tetramethyldiaminobenzophenone furnishes auramine. "Alizarin yellows A and C," when treated in this way, yield products giving yellow and olive tints with the usual mordants, which are different from those given by the original dyes.

When alizarin is fused with ammonium thiocyanate in place of ammonium carbonate, or sulphur is added to a mixture of alizarin, glycerol, and the organic ammonium salt used to produce alizarinimide in the above reaction, the sulphur appears to enter into combination and to modify the tinctorial properties of the alizarinimide formed. T. A. H.

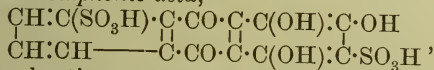
**Preparation of Hydroxyanthraquinonesulphonic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 172688. Compare Abstr., 1905, i, 146).—The treatment of anthraquinone- $\alpha$ -sulphonic acid with fuming sulphuric acid containing a high percentage of sulphur trioxide leads to the introduction of hydroxyl groups into the anthracene nucleus. It is now found that the same result is obtained when acid containing less than 45 per cent. of sulphur trioxide is employed either with or without boric acid. Small quantities of mercury salts are found in many cases to accelerate the oxidation.

*Alizarin-3:5-disulphonic acid,*



is produced by heating at 130—135° a mixture of potassium anthraquinone- $\alpha$ -sulphonate, boric acid, and fuming sulphuric acid containing 40 per cent. of sulphur trioxide. The *acid potassium* salt of alizarin-3:5-disulphonic acid crystallises on pouring the acid fusion into ice-cold water, whilst the quinizarin- $\alpha$ -sulphonic acid also produced in this reaction remains in solution and is precipitated with sodium chloride. Alizarin-3:5-disulphonic acid, when heated at 180° with 70 per cent. sulphuric acid, yields alizarin-5-sulphonic acid.

*Purpurin-3:8-disulphonic acid,*



is produced by heating potassium anthraquinone-1:5-disulphonate with boric acid and fuming sulphuric acid (40 per cent.  $\text{SO}_3$ ), under 6 to 7 atmospheres pressure. When poured into water, the fusion yields the *acid potassium* salt of this acid, which, when crystallised from dilute hydrochloric acid, separates in yellowish-red leaflets or prisms having a bronzy lustre. When heated at 180° with 70 per cent. sulphuric acid, the foregoing disulphonic acid furnishes purpurin- $\alpha$ -sulphonic acid; if a mercury salt is added, purpurin itself is formed.

Other di- and tri-hydroxyanthraquinonesulphonic acids can be prepared similarly by the foregoing process, and the properties of some of these products are tabulated in the patent.

G. T. M.

**Preparation of Chlorinated Quinazarins.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172105).—Chlorinated quinazarins may be prepared by condensing quinol with those chlorophthalic acids which contain not more than one halogen atom in an ortho-position with respect to the carboxyl groups.

Quinol and 4:5-dichlorophthalic anhydride are heated at 155—160° for four hours in concentrated sulphuric acid, either alone or with the addition of boric acid; the product is poured into water, dissolved in an aqueous alkali hydroxide and reprecipitated by dilute acid. When crystallised from glacial acetic acid, it separates in brownish-red leaflets melting at 255°. Its solutions are bluer than those of quinazarin itself; that in concentrated sulphuric acid assumes a yellow fluorescence on the addition of boric acid.

*5-Chloroquinazarin*, obtained from quinol and 3-chlorophthalic acid, crystallises from glacial acetic acid in brownish-red needles melting at 240°.

G. T. M.

**Bluish-green Colouring Matters of the Anthracene Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 172575).—When dinitroanthrarufindisulphonic acid is reduced with alkali sulphides in alkaline solutions, the reaction leads readily to the formation of diaminoanthrarufindisulphonic acid. If, however, the nitrosulphonic acid is reduced with sulphide in neutral solution, then beside the diamino-derivative a new product is formed, and this is obtained exclusively when alkali hydrosulphide is used instead of a sulphide. Although the exact nature of this new substance has not yet been ascertained, it is probably a partial reduction product such as a hydroxylamino- or a nitroamino-derivative, but it has not yet been

found possible to complete its reduction to diaminoanthrarufindisulphonic acid (Alizarinsaphirol  $\beta$ ). The new product differs from the diamino-derivative in several of its colour reactions and also in tinctorial properties. These characteristic differences are arranged in the patent in tabular form.

G. T. M.

**Preparation of *p*-Nitro-derivatives of the  $\alpha$ -Hydroxyanthraquinones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 170728).—The nitration of the  $\alpha$ -hydroxyanthraquinones themselves leads to the production of a complex mixture of isomerides of which only the *p*-nitro-derivatives are of technical importance. It is therefore preferable to nitrate the aryl ethers of the  $\alpha$ -hydroxyanthraquinones, as on hydrolysis the nitro-compounds thus obtained yield exclusively the required *p*-nitro-derivatives.

The diphenyl ether of anthrarufin on nitration yields the hexanitro-compound, 
$$\begin{array}{c} \text{CH}:\text{C}[\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2]\cdot\text{C}\cdot\text{CO}\cdot\text{C}\cdot\text{C}(\text{NO}_2)=\text{CH} \\ \text{CH}:\text{C}(\text{NO}_2)\text{---}\text{C}\cdot\text{CO}\cdot\text{C}\cdot\text{C}[\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2]\cdot\text{CH} \end{array}$$
 which on alkaline hydrolysis gives rise to 2:4-dinitrophenol and *p*-dinitroanthrarufin.

The diphenyl ester of chrysazin gives a similar hexanitro-compound which on hydrolysis furnishes 2:4-dinitrophenol and *p*-dinitrochrysazin.

G. T. M.

**Preparation of Dichlorochrysazin.** R. WEDEKIND & Co. (D.R.-P. 172300).—Chrysazin is not affected by chlorinating agents at 100°, but when 10 parts of this substance are suspended in 1000 parts of concentrated sulphuric acid diluted with their own weight of water and heated at 125°, while a solution of 20 parts of potassium chlorate and 80 parts of sodium chloride also dissolved in the same quantity of water is slowly added, chlorination takes place readily, and *pp*-dichlorochrysazin separates in well-defined orange-coloured crystals.

G. T. M.

**Preparation of 1:2:2':1'-Anthrazine.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 172684).—1:2:2':1'-Anthrazine, which was formerly obtained with great difficulty by the reduction of indanthrene, a substance formed by fusing  $\beta$ -aminoanthraquinone with alkali hydroxides, is now prepared by heating  $\beta$ -anthramine with a mixture of sodium and potassium hydroxides at 220–230° in the absence of air. The anthrazine, which forms a dark layer on the alkali, is easily separated and obtained pure by recrystallisation from nitrobenzene.

G. T. M.

**Thioborneol.** WALTHER BORSCHÉ and W. LANGE (*Ber.*, 1906, 39, 3268).—Thioborneol, described recently by the authors (this vol., i, 679), had been obtained previously by Wuyts (*Abstr.*, 1903, i, 428).

C. S.

**Artificial Production of Camphor from Turpentine Oil.** OTTO SCHMIDT (*Chem. Centr.*, 1906, ii, 722; from *Chem. Ind.*, 29, 241–244).—The yield of camphor obtained by initially treating the



crude oil with hydrochloric acid is very nearly the same (25 per cent.) as that obtained by the use of oxalic or salicylic acid. The conversion of pinene into bornyl and isobornyl esters is readily effected by means of *o*-chlorobenzoic acid, which is more stable than salicylic acid and, therefore, to be preferred to the latter.

H. M. D.

**The Isolation of  $\psi$ -Ionone Hydrate and an Isomeride.** P. COULIN (D.R.-P. 172653).—When moderately concentrated acids act on  $\psi$ -ionone even at the ordinary temperature, there is produced, together with ionone, hydrocarbons and tarry matters, a certain amount of substances, the boiling points of which are higher than those of ionone,  $\psi$ -ionone, or the hydrocarbons. It is now shown that this mixture contains  $\psi$ -ionone hydrate and an isomeride,  $C_{13}H_{22}O_2$ , and that these two compounds can be separated by means of alkali sulphites, in solutions of which the  $\psi$ -ionone hydrate readily dissolves, whilst its isomeride is insoluble. This isomeric substance is a viscid oil boiling at  $166.8^\circ$  to  $169.8^\circ$  under 10.5 mm. pressure and having a refractive index 1.50647 at  $21^\circ$ ; it slowly solidifies to a crystalline mass melting at  $80^\circ$ ; its *semicarbazone*, which is formed quantitatively, crystallises readily and melts and decomposes at  $228^\circ$ .

The  $\psi$ -ionone hydrate is isolated from the sodium sulphite solution by making this strongly alkaline and extracting with ether or benzene; it boils at  $180$ — $182^\circ$  under 12 mm. pressure, and has a sp. gr. 0.954 at  $15^\circ$  and  $n_D$  1.53322 at  $20^\circ$ .

G. T. M.

**Oils from Conifers.** R. E. HANSON and E. N. BABCOCK (*J. Amer. Chem. Soc.*, 1906, 28, 1198—1201).—The following volatile oils, with the exception of the first two and the last, are now described for the first time.

The leaves of the black spruce (*Picea Mariana*) yield 0.57 per cent. of an oil which has a sp. gr. 0.9274 at  $19^\circ$ .

Samples of oil distilled from the leaves and twigs of the hemlock (*Tsuga canadensis*) were obtained in yields of 0.4 and 0.46 per cent., and had a sp. gr. 0.9238 and 0.9273 respectively at  $15^\circ$ .

The leaves of the cat spruce (*Picea canadensis*) yield 0.103 per cent. of an oil which has a sp. gr. 0.9216 at  $15^\circ$ , and contains 25.7 per cent. of esters (calculated as bornyl acetate).

The leaves of the red spruce (*Picea rubens*) furnish 0.204 per cent. of an oil which has an agreeable odour and a sp. gr. 0.9539 at  $16^\circ$ , and contains 7.76 per cent. of borneol and 66.2 per cent. of bornyl acetate.

The leaves and twigs of the American larch (*Larix americana*) yield 0.149 per cent. of an oil which has a sp. gr. 0.8816 at  $15^\circ$  and consists chiefly of pinene together with 15.1 per cent. of esters (calculated as bornyl acetate).

The cones of *Picea rubens* yield 0.38 per cent. of a golden-yellow oil which has a sp. gr. 0.8600 at  $15^\circ$ .

The cones of *Picea canadensis* yield 0.25 per cent. of a yellow oil which has a limonene-like odour and a sp. gr. 0.899 at  $15^\circ$ .

The leaves and twigs of the pitch pine (*Pinus rigida*) furnish a

very small quantity (0.2 c.c. from 12 kilograms) of a yellow oil which has an extremely pungent odour.

The red pine (*Pinus resinosa*) yields about 0.001 per cent. of a pungent, brown oil.

The leaves and twigs of *Juniperus communis* furnish 0.15–0.18 per cent. of a light yellow oil which has a sp. gr. 0.8531 at 20°.

The oil distilled from the leaves of *Juniperus virginiana* has a sp. gr. 0.900 at 16°. E. G.

**Action of Phenols and Naphthalene on Copals.** CH. COFFIGNIER (*Bull. Soc. chim.*, 1906, [iii], 35, 762–767).—Madagascar copal and the products obtained from it (1) by “running” by the usual pyrogenetic process and (2) by heating it at 260–290° in closed vessels with naphthalene by Terrisse’s process (*Brev. français*, 334, 300, Oct. 1904) have been compared. The product obtained by “running” copal in the usual way is less soluble in alcohols, acetone, and amyl acetate, and more soluble in ether, turpentine oil, benzene, and chloroform than the crude copal. That prepared by Terrisse’s process, when compared with the crude copal, is slightly less soluble in methyl alcohol, more soluble in chloroform, ether, turpentine oil, and benzene, whilst the solubility in ethyl alcohol and acetone remains practically unchanged.

Both products show a higher specific gravity, a lower melting point, a lower acid number, and a lower Köttstorfer number than the raw copal. There is no loss of weight when Terrisse’s process is used and the product is lighter in colour than that obtained by the usual method. T. A. H.

**American Colophony.** PAUL LEVY (*Ber.*, 1906, 39, 3043–3046).—The abietic acid,  $C_{19}H_{29} \cdot CO_2H$ , obtained by the author from American colophony, although identical crystallographically with the acid prepared by other workers, differs from this in melting point and in its capacity for crystallising. American colophony, on distillation under reduced pressure, yields an oily hydrocarbon,  $C_{19}H_{30}$ , which, after purification, boils at 210–211° under 26.5 mm. pressure, and has a sp. gr. 0.977 at 20°. This substance is readily soluble in ether and benzene, and is not very miscible with alcohol.

The foregoing hydrocarbon is undoubtedly identical with Deville, and Bischoff and Nastvogel’s “colophene,” and with Easterfield and Bagley’s “abietene” (compare *Trans.*, 1904, 85, 1238).

Abietic acid, when treated with phosphorus pentachloride or thionyl chloride, furnishes an acid chloride, which, however, was not isolated in a state of purity, since it decomposes on distillation under reduced pressure. By repeated fractionation, an oily fluorescent hydrocarbon was obtained from the products of this decomposition, which boiled at 200–202° under 17 mm. pressure. To this substance, which is formed in accordance with the following equation,  $C_{19}H_{29} \cdot COCl = C_{19}H_{28} + CO + HCl$ , the author gives the name abietin. Towards organic solvents it behaves like abietene, and appears to correspond with the substance obtained by Kraemer and Spilker by the dry distillation of colophony (compare *Abstr.*, 1900, i, 150). G. T. M.

**The Identity of Thudichum's Phrenosin and Thierfelder's Cerebron.** WILLIAM J. GIES (*J. Biol. Chem.*, 1906, 2, 159—182).—Thierfelder does not admit the identity of these two substances, although he admits on precisely the same grounds the identity of his cerebron with Gamgee's pseudo-cerebrin. The present paper is partly an historical literary retrospect into the subject, and is largely polemical. The identity of the two materials is maintained, as Gies and Posner originally stated.

W. D. H.

**Fern Secretions. I. Glandular Secretions of *Gymnogramme chrysophylla* and *G. calomelanos*.** WILHELM ZOPF (*Chem. Centr.*, 1906, ii, 690—691; from *Ber. Deut. bot. Ges.*, 24, 264—272).—From the extract obtained by momentary immersion of the fronds of *Gymnogramme chrysophylla* in ether, two substances have been isolated: a colourless, neutral wax, which melts at 63—64°, and *gynogrammen*,  $C_{18}H_{18}O_5$ , which crystallises in red, plate-like prisms, probably monoclinic, melts at 159°, and has an aromatic odour. It is insoluble in water, but dissolves readily in cold acetone and alcohol. It is decomposed by alkali solutions, gives a red colour with ferric chloride, and dissolves in concentrated sulphuric acid with an intense golden-yellow colour. On boiling with ethyl alcohol, it yields *gymnogrammidin*, which forms colourless needles melting at 114—115°.

From *Gymnogramme calomelanos*, a colourless substance, *calomelanen*,  $C_{20}H_{22}O_6$ , has been obtained; it has a camphoraceous odour, crystallises in small needles, melts at 141—142°, and dissolves readily in ethyl ether and ethyl alcohol. It gives a red colour with ferric chloride, and dissolves in concentrated sulphuric acid with a yellow colour. Boiling water decomposes it, and yields a volatile substance, which also has an odour resembling that of camphor.

H. M. D.

**Brazilin and Hæmatoxylin.** JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1906, 27, 743—771. Compare *Abstr.*, 1903, i, 270, 713; 1904, i, 81, 333; 1905, i, 605; this vol., i, 198).—The authors compare their structural formula for brazilin with that suggested by Pfeiffer (*Chem. Zeitschr.*, 1904, 3, 390, 420) which closely resembles it.

When heated with acetic anhydride, sodium acetate, and zinc dust, the phenylhydrazine derivative of tetramethylhæmatoxyloxyne forms a reduced *acetyl* derivative,  $C_{24}H_{16}O_2N_2(OMe)_4$ , which crystallises in white needles and melts at 188—192°.

[With ROBERT FISCHER.]—The isomeride obtained from tetramethylhæmatoxyloxyne is readily soluble in aqueous alkali hydroxides, and can be titrated sharply with phenolphthalein as indicator. When boiled with alcoholic potassium hydroxide or with alcoholic hydrogen chloride, it forms a *methyl ether*,  $C_{16}H_7O_2(OMe)_5$ , which crystallises from alcohol, melts at 99—102°, and when boiled with aqueous-alcoholic potassium hydroxide is hydrolysed, forming the isomeride of tetramethylhæmatoxyloxyne melting at 169—171°. The methyl ether remains unchanged when boiled with acetic anhydride and sodium acetate; in alcoholic solution, it forms with concentrated sulphuric acid a red ring which disappears on shaking, but if sufficient acid is added the whole



mixture becomes red, and the methyl ether is converted into  $\beta$ -dehydrotetramethylhæmatoxylin. The isomeride melting at 169—171° does not react with hydroxylamine or with phenylhydrazine, and is not reduced by zinc dust in boiling glacial acetic acid solution.

[With WOLFGANG KLUGER.]—Acetyltrimethylbrazilin has  $[\alpha]_D + 128^\circ 14'$  at 20° or  $+ 125^\circ 54' 50''$  at 22°. Acetyltetramethylhæmatoxylin has  $[\alpha]_D + 151^\circ 28' 32''$  to  $+ 152^\circ 11' 54''$  at 20°. As tetra-acetyl-brazilin prepared by acetylation of brazilin has  $[\alpha]_D + 76^\circ 24' 31''$ , and that prepared by simultaneous reduction and acetylation of brazilin has  $[\alpha]_D + 75^\circ 26' 30''$ , von Kostanecki and Feuerstein's formulæ for brazilin, which has one, and for brazilin, which has no asymmetric carbon atom, are probably incorrect. Almost all reactions of brazilin or its alkyl derivatives lead directly to the formation of inactive substances.

The triacetyl compound,  $C_{16}H_9O(OAc)_3$  (Abstr., 1902, i, 482), and tetra-acetyl compound,  $C_{16}H_8(OAc)_4$  (Abstr., 1901, i, 478), obtained by simultaneous reduction and acetylation of brazilin, have  $[\alpha]_D - 30^\circ 14'$  and  $+ 3^\circ 22' 46''$  respectively.

Two preparations of trimethylbrazilone obtained by oxidation of trimethylbrazilin with chromic acid in acetic acid solution have  $[\alpha]_D + 1^\circ 34' 4''$  and  $- 1^\circ 10' 33''$  respectively. Brazilinic acid has  $[\alpha]_D + 13^\circ 53''$ .

The formation of  $\gamma$ -tetramethyldehydrobrazilin by heating trimethylbrazilone with methyl iodide and potassium hydroxide on the water-bath is confirmed (compare Abstr., 1902, i, 482; 1904, i, 908).

[With ADOLF MAYRHOFFER.]—The action of diacetylorthonitric acid (Pictet and Genequand, Abstr., 1902, i, 584) on  $\psi$ -trimethylbrazilone (the isomeride obtained by the action of sulphuric acid on trimethylbrazilone) in cooled glacial acetic acid solution leads to the formation of *nitro- $\psi$ -trimethylbrazilone*,  $C_{16}H_9O_3(OMe)_3 \cdot NO_2$ , which separates from ethyl acetate in yellowish-brown crystals, melts at 210—214°, is sensitive to light, and when boiled with acetic anhydride and sodium acetate yields a *product*, probably *nitro- $\beta$ -acetyltrimethyldehydrobrazilin*,  $C_{18}H_8O_3(OMe)_3 \cdot NO_2$ , forming glistening, yellow crystals and not melting at 260°.

When nitrated in the same manner, the monomethyl ether of  $\psi$ -trimethylbrazilone yields the *nitro-derivative*,  $C_{16}H_7O_2(OMe)_4 \cdot NO_2$ , which crystallises from alcohol, melts at 196—198°, and does not react with diazomethane.

When treated with twice its weight of diacetylorthonitric acid in 10 vols. of glacial acetic acid,  $\psi$ -tetramethylhæmatoxylone (the isomeride of tetramethylhæmatoxylone) yields a mononitro-derivative,  $C_{16}H_7O_3(OMe)_4 \cdot NO_2$ , which crystallises in long, glistening, yellow needles and melts at 221—222°. On acetylation this yields a *dehydroacetate*,  $C_{18}H_7O_3(OMe)_4 \cdot NO_2$ , which crystallises in long, sulphur-yellow needles and melts at 198—200°, together with a small amount of a sparingly soluble *isomeride*, which crystallises in slender, light yellow needles, melts and decomposes at 289—291°, has a low specific gravity, and is formed on treatment of the product melting at 198—200° with acetic anhydride and sulphuric acid.

Nitration of  $\psi$ -tetramethylhæmatoxylone with four times its weight

of diacetylorthonitric acid in four vols. of cooled glacial acetic acid leads to the formation of the *dinitro*-derivative,  $C_{16}H_6O_3(OMe)_4(NO_2)_2$ , which forms yellow crystals, melts and decomposes at  $173-176^\circ$ , and yields a *dehydroacetyl* derivative,  $C_{18}H_6O_3(OMe)_4(NO_2)_2$ ; this crystallises in slender, yellow needles and melts and decomposes at  $266-268^\circ$ .

Nitration of the methyl ether of  $\psi$ -tetramethylhæmatoxylone by means of diacetylorthonitric acid, leads to the formation of three isomeric *mononitro*-derivatives,  $C_{16}H_6O_3(OMe)_5 \cdot NO_2$ ; the isomeride melting at  $131-136^\circ$  forms slender, yellow crystals and is prepared also by the action of diazomethane on nitro- $\psi$ -tetramethylhæmatoxylone; the second melts at  $162-165^\circ$  and forms short, slender, yellow needles, whilst that melting at  $206-207^\circ$  crystallises in long, slender, yellow needles.

G. Y.

**Yellow Colouring Matter in Surinam Greenheart.** W. H. BLOEMENDAL (*Chem. Centr.*, 1906, ii, 527; from *Pharm. Weekblad*, 1906, 43, 678-686).—In the author's opinion, the dyes variously described as Tecomin, Grönhartin, Bethabarra colouring matter, Taigu-Lapachoic acid, and Lapachol are all identical with the yellow, crystalline substance of the formula  $C_{15}H_{14}O_3$ , obtained from the wood of the *Bignonia* and described first by Paterno and later by Hooker (*Trans.*, 1896, 69, 1355).

P. H.

**Colouring Matters of Phæophyceæ.** M. TSWETT (*Chem. Centr.*, 1906, ii, 529-530; from *Ber. Deut. bot. Ges.*, 1906, 24, 235-244).—The production of the brown substance, phycophæin, is attributed to the oxidation of colourless chromogen. The following properties are mentioned as characteristic of carotin; unlike the xanthophylls or fucoxanthin it is more soluble in light petroleum, benzene, or carbon disulphide than in strong alcohol and is not adsorbed from a light petroleum solution by powdered calcium carbonate; moreover, neither the crystallised substance nor an alcoholic solution is turned blue by hydrochloric acid, and a solution in light petroleum shows three absorption bands, two at  $492-475 \mu\mu$  and one at  $460-445 \mu\mu$ . In addition to carotin and fucoxanthin, the author has isolated from fucus extract a substance, *fucoxanthophyll*, which closely resembles fucoxanthin in its solubilities and its spectroscopic behaviour, but optical properties of which remain unchanged by treatment with sodium hydroxide. Chlorophyllin  $\gamma$ , which is also contained in the seaweed, is insoluble in light petroleum, but is soluble in alcohol or ether; when dissolved in the latter solvent, it shows absorption bands at  $638-622 \mu\mu$ ,  $588-575 \mu\mu$ , and  $465-440 \mu\mu$ . The natural brownish-green colour of algæ is produced as a result of the mixture of all the above-mentioned colouring matters. The destruction of the fucoxanthin is the cause of algæ turning green.

P. H.

[**Action of Formaldehyde on Gallocyanin.** FARBWERKE VORM. L. DURAND, HUGUENIN & Co. (D.R.-P. 171459).—Gallocyanin and formaldehyde condense to form a new colouring matter which is readily reduced with reducing agents such as zinc dust and hydro-

chloric acid, sodium hyposulphite or sodium sulphide to form a new leuco-base, which is obtained in the form of grey or yellow hydrochloride. This salt dissolves in water to a brownish-yellow solution; in concentrated sulphuric acid, it exhibits a blue-reddish-yellow dichroism. The leuco-base is precipitated by alkalis as a greenish-yellow, flocculent precipitate, which oxidises on exposure to air. The addition of manganese dioxide to an acid solution of the leuco-base develops an intense greenish-blue coloration. The leuco-base dyes wool in an acid bath. G. T. M.

**Conjugated Dionium Ring Systems.** HERMAN DECKER (*Ber.*, 1906, 39, 3069—3071. Compare Abstr., 1905, i, 667).—Attention is called to the facility with which certain cyclic complexes of high molecular weight undergo a reversible process of oxidation and reduction. Dinaphthylene dioxide dissolves in concentrated sulphuric acid to a light yellow solution in the absence of oxygen. In the presence of this or other oxidising agent, the colour changes to dark blue, due to the dioxonium salt (compare Bünzly and Decker, Abstr., 1905, i, 884). A small quantity of water added to the yellow solution precipitates the original compound, but larger quantities can be added to the blue solution, changing its colour first to red (carbinolmon-oxonium salt), and then precipitating the yellow dicarbinol base. The blue solution is readily changed by reducing agents to the yellow, fluorescent solution of dinaphthylene dioxide.

Similar relations have been observed between isologous coeroxene and between coerthiene derivatives (compare this vol., i, 687).

C. S.

**Researches on Furans.** 2:5-Dicarbethoxy-3:4-diketotetrahydrofuran. I. TREAT B. JOHNSON and CARL O. JOHNS (*Amer. Chem. J.*, 1906, 36, 290—294).—*Ethyl 3:4-diketotetrahydrofuran-2:5-dicarboxylate*,  $O \begin{array}{l} \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \\ \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \end{array}$ , obtained in quantitative yield by

the condensation of ethyl oxalate with ethyl diglycollate, forms stout, prismatic crystals, melts at 189°, and is very soluble in hot alcohol; the *sodium* salt is obtained as a white powder. E. G.

**Rhodamines.** II. EMILIO NOELTING and KARL DZIEWOŃSKI (*Ber.*, 1906, 39, 2744—2749. Compare Abstr., 1905, i, 935).—*Tetraethylrhodamine silver nitrate*,  $\text{C}_{28}\text{H}_{30}\text{O}_3\text{N}_2 \cdot \text{AgNO}_3$ , obtained by mixing alcoholic solutions of the components, crystallises in glistening, bluish-green plates. *apoRhodamine* forms a similar compound which is decomposed when shaken with cold water.

The esters of aporhodamine are prepared readily by the usual catalytic method, using hydrogen chloride. *Ethylaporhodamine hydrochloride*,  $\text{C}_{25}\text{H}_{24}\text{O}_3\text{NCl} \cdot 5\text{H}_2\text{O}$ , crystallises in pale red needles with a golden lustre, melts at 95°, and is not hydrolysed by boiling water. When decomposed by aqueous solutions of alkalis, the hydrochloride yields *aporhodamine*, but with the theoretical amount of cold alcoholic potassium hydroxide, it yields the *carbinol ether* of the

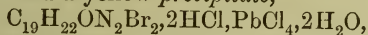


ester,  $O < \begin{smallmatrix} C_6H_3Me \\ C_6H_3(NMe_2) \end{smallmatrix} > C(OEt) \cdot C_6H_4 \cdot CO_2Et$ , in the form of colourless prisms melting at  $105^\circ$ . With hydrochloric acid, ethyl alcohol is eliminated and the hydrochloride of the ester regenerated.

apoRhodamine-imide,  $O < \begin{smallmatrix} C_6H_3(NMe_2) \\ C_6H_3Me \end{smallmatrix} > C < \begin{smallmatrix} NH \\ C_6H_4 \end{smallmatrix} > CO$ , obtained by the action of hot alcoholic ammonia on the hydrochloride of the ester, crystallises in large, glistening prisms, melts at  $227^\circ$ , and contains a half molecule of alcohol of crystallisation. It dissolves in hot dilute acids, yielding colourless solutions. J. J. S.

Compounds of the Hydrochlorides of the Alkaloids with the Chlorides of the Heavy Metals and the Corresponding Bromine Compounds. A. CHRISTENSEN (*J. pr. Chem.*, 1906, [ii], 74, 161—187. Compare Classen and Zahorsky, *Abstr.*, 1893, ii, 464; Wells, *ibid.*, 523; Goebbels, *Abstr.*, 1895, i, 390).—Lead tetrachloride combines with quinine hydrochloride in hydrochloric acid solution to form an amorphous *additive* compound, which gradually becomes yellow and crystalline: with cinchonidine hydrochloride forming a yellow *precipitate* consisting of small prisms, and with cinchonine hydrochloride forming a *precipitate* consisting of rosettes of microscopic, yellow needles. These three additive compounds readily decompose, yielding an odour of chlorine.

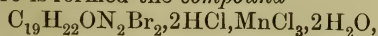
In the same manner, from  $\alpha$ -cinchonidine dibromide hydrochloride there is formed the compound  $C_{19}H_{22}ON_2Br_2 \cdot 2HCl \cdot PbCl_4 \cdot 2H_2O$ , which is obtained in yellow, microscopic prisms and does not decompose when dried. The precipitate formed from  $\beta$ -cinchonidine dibromide hydrochloride is amorphous. With  $\alpha$ -cinchonine dibromide hydrochloride there is formed a yellow *precipitate*,



which consists of concentric aggregates of microscopic needles; the *precipitate* formed with  $\beta$ -cinchonine dibromide hydrochloride is yellow and amorphous.

The action of potassium bromide solution on the freshly-prepared double salt of  $\alpha$ -cinchonidine dibromide hydrochloride and lead tetrachloride leads to the formation of a *product* which crystallises in quadratic, yellow leaflets or prisms, and when treated with water yields lead bromide. The *product* of the action of lead bromide and bromine on  $\beta$ -cinchonidine dibromide in hydrobromic acid solution behaves as a mixture of the compounds  $C_{19}H_{22}ON_2Br_2 \cdot 2HBr \cdot PbBr_4$  and  $C_{19}H_{22}ON_2Br_2 \cdot 2HBr \cdot Br_2$ .

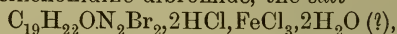
Double salts of manganese trichloride (compare Rice, *Trans.*, 1898, 73, 258; Meyer and Best, *Abstr.*, 1900, ii, 77) were prepared by adding a solution of the alkaloid in glacial acetic acid solution to manganese dioxide stirred into glacial acetic acid, and adding the calculated amount of 40 per cent. hydrochloric acid or passing hydrogen chloride into the mixture. With  $\alpha$ -cinchonidine dibromide hydrochloride there is formed the *compound*



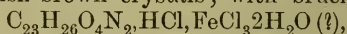
which forms green, microscopic crystals, decomposes and becomes brown on addition of water, and reacts with potassium iodide and hydro-

chloric acid, yielding the periodide. The similarly-constituted *salt* with  $\beta$ -cinchonidine dibromide hydrochloride contains  $\text{H}_2\text{O}$ , is obtained as a light green powder consisting of concentric aggregates of small crystals, and when exposed to air decomposes rapidly losing chlorine. With  $\alpha$ - and  $\beta$ -cinchonine dibromide there are formed green, amorphous, hygroscopic *precipitates*, which decompose, losing chlorine in a desiccator.

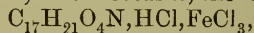
The following double salts are formed by addition of alkaloids to ferric chloride in hydrochloric acid solution (Borsbach, *Abstr.*, 1890, 643). With quinine, the salt  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot 2\text{HCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ , which is obtained as a yellow, crystalline powder consisting of microscopic, hexagonal prisms; with cinchonidine, the *compound*  $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot 2\text{HCl} \cdot \text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ , which crystallises in microscopic, yellow prisms; with cinchonine, the *salt*  $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot 2\text{HCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$  (?), which separates in sheaves of microscopic, yellow, rectangular crystals; with  $\alpha$ -cinchonidine dibromide, the *salt*



which crystallises in sheaves of long needles; with strychnine, the *salt*  $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2 \cdot \text{HCl} \cdot \text{FeCl}_3$ , which forms a precipitate consisting of microscopic, yellowish-brown crystals; with brucine, the *salt*



which forms a heavy, greyish-brown precipitate, gradually changing into spherical crystals; with cocaine, the *salt*



which separates as a sulphur-yellow, micro-crystalline powder; with morphine, the *compound*  $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N} \cdot \text{HCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ , crystallising in sheaves of microscopic, brown needles, giving the characteristic blue coloration obtained on addition of ferric chloride to morphine, and decomposing with formation of morphine hydrochloride when recrystallised from hydrochloric acid; with caffeine, the *salt*  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4 \cdot \text{HCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ , forming microscopic, hexagonal, short crystals; with pyridine, the *compound*  $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl} \cdot \text{FeCl}_3$ , crystallising in yellow, pointed, tetragonal prisms; with quinoline, the *salt*  $\text{C}_9\text{H}_7\text{N} \cdot \text{HCl} \cdot \text{FeCl}_3$ , which crystallises in microscopic, long, pointed prisms and is readily soluble in water.

Similar double salts of the alkaloids are formed with ferric bromide and hydrobromic acid; these are less stable than the corresponding chlorine compounds and can be isolated in a state of purity only in exceptional cases. With cinchonidine, the *salt*  $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot 2\text{HBr} \cdot \text{FeBr}_3 \cdot 2\text{H}_2\text{O}$  separates as an orange-red, crystalline precipitate; the cinchonine *salt* is thrown down as an amorphous precipitate, changing gradually into small, yellow prisms; the quinine *salt* is obtained as a red, amorphous precipitate; the caffeine *salt*,  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4 \cdot \text{HBr} \cdot \text{FeBr}_3 \cdot \text{H}_2\text{O}$ , forms a reddish-brown, micro-crystalline powder; the quinoline *salt*,  $\text{C}_9\text{H}_7\text{N} \cdot \text{HBr} \cdot \text{FeBr}_3$ , separates in reddish-brown, microscopic, hexagonal crystals. G. Y.

**Clavine, a New Constituent of Ergot.** ERNST VAHLEN (*Chem. Centr.*, 1906, ii, 690; from *Arch. exper. Path. Pharm.*, 55, 131—163).—*Clavine*,  $\text{C}_{11}\text{H}_{22}\text{O}_4\text{N}_2$ , is obtained when an aqueous extract of ergot is precipitated with a hot saturated solution of barium hydroxide, the

barium removed from the solution by carbon dioxide, and the concentrated filtrate extracted with hot alcohol. It forms elongated needles or small, nacreous, rhombic plates and melts at  $262\text{--}263^\circ$  in a closed tube. When heated carefully it sublimes, forming star-shaped aggregates of small prisms. It dissolves readily in water and is not precipitated by alkali hydroxides or carbonates. It is only slightly soluble in ethyl alcohol, and insoluble in ether, ethyl acetate, or light petroleum.

In aqueous solution it is split up into two substances having approximately the same molecular weight. By addition of copper hydroxide or a solution of copper acetate, the copper salts of two acids, both containing nitrogen, are formed, one of which is soluble, the other insoluble in water.

The aqueous solution of clavine has an insipid taste and yields no precipitate with the alkaloid reagents. It is much more soluble in acid and alkaline solutions than in water. On evaporation of a hydrochloric acid solution, delicate prisms of the *hydrochloride*,  $\text{C}_{11}\text{H}_{22}\text{O}_4\text{N}_2 \cdot 2\text{HCl}$ , are obtained. It exerts a specific action on the uterus causing this to contract.

H. M. D.

**Morphine. VIII. Trihydroxyphenanthrene from Hydroxycodine.** LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1906, 39, 3252—3255).—The methoxydiacetoxyphenanthrene obtained from hydroxycodine (compare Knorr and Schneider, this vol., i, 449) is oxidised by chromic and glacial acetic acids to Vongerichten's acetyl-methylmorpholquinone (*Abstr.*, 1898, i, 281). From this it follows that the hydroxyl group, introduced into codeine by oxidation, must be situated in position 9 or 10, and, moreover, that as this hydroxyl group exhibits an alcoholic and not a phenolic function, consequently the "bridge" carbon atoms of the phenanthrene nucleus, not only in codeine, but also in methylmorphimethine, must be dihydrogenated. This result renders untenable Freund's formulæ for thebaine and codeine (*Abstr.*, 1905, i, 918; this vol., i, 303) and Pschorr's "pyridine" formula for morphine (*Abstr.*, 1903, i, 193).

Methoxydiacetoxyphenanthrene has been obtained by Pschorr from dichloromethylmorphimethine (see following abstract). C. S.

**Halogen Derivatives of Morphine and Codeine, and their Degradation.** ROBERT PSCHORR (*Ber.*, 1906, 39, 3130—3139).—[With HERMANN VOGTHER.]—*Chloromorphide*,  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{NCl}$ , resulting from the action of hydrogen chloride on morphine at the ordinary temperature, melts at  $192^\circ$  (corr.); the *methiodide*,  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{NCl} \cdot \text{MeI}$ , melts at  $207^\circ$  (corr.).

*Bromomorphide hydrobromide*,  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{NBr} \cdot \text{HBr}$ , obtained by treating morphine with phosphorus pentabromide and subsequently with hydrogen bromide, decomposes at  $196^\circ$ ; the *base*,  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{NBr}$ , forms needles and melts at  $170^\circ$ , the *methiodide* at  $200^\circ$ , and the *anilino-carboxylic ester*,  $\text{C}_{24}\text{H}_{23}\text{O}_3\text{N}_2\text{Br}$ , at  $204^\circ$ .

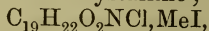
*Bisthiomorphide*,  $(\text{C}_{17}\text{H}_{19}\text{O}_2\text{NS})_2$ , is prepared by heating chloro- or bromo-morphide with alcoholic potassium hydrosulphide; it melts at  $201^\circ$  and forms a *methiodide*,  $(\text{C}_{19}\text{H}_{23}\text{O}_2\text{NSI})_2$ , which melts at  $253^\circ$  and



is also obtained from *bisthiocodide*,  $(C_{18}H_{20}O_2NS)_2$ , which is soluble in alkali and melts at  $200^\circ$  (corr.). *Ethylthiocodide*,  $C_{20}H_{25}O_2NS$ , obtained by heating bromocodide with alcoholic sodium mercaptide in an atmosphere of hydrogen, melts at  $145^\circ$  (corr.).

[With E. KUHTZ and HEINRICH ROTH.]—*Chlorocodide methiodide*,  $C_{19}H_{23}O_2NCl$ ,

decomposes at  $166$ — $167^\circ$  and does not yield chloromethylmorphimethine by heating with sodium hydroxide. The *hydrochloride* of the chlorinated methine base,  $C_{19}H_{22}O_2NCl \cdot HCl$ , results, however, when  $\alpha$ -methylmorphimethine is treated with phosphorous chloride in chloroform; it crystallises in tufts of needles and melts at  $177$ — $178^\circ$  (corr.). The base has not been obtained crystalline; the *methiodide*,

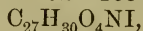


forms slender needles and melts at  $163^\circ$  (corr.). In the absence of a solvent, the preceding reaction results in the formation of the compound  $C_{19}H_{22}O_2N \cdot O \cdot P(OH)_2 \cdot HCl$ .

By heating with acetic anhydride, chloromethylmorphimethine hydrochloride yields Knorr's acetylmethyl-dihydroxyphenanthrene (Abstr., 1889, 905). The nitrogenous fission product is, according to the conditions of the decomposition, either methyl- $\beta$ -hydroxyethylamine or dimethyl- $\beta$ -hydroxyethylamine and a base having the composition of tetramethylethylenediamine.

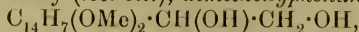
*Dichloromethylmorphimethine*,  $C_{19}H_{23}O_3NCl_2$ , obtained as the hydrochloride by the action of phosphoric chloride on  $\alpha$ -methylmorphimethine in chloroform, decomposes at  $180$ — $181^\circ$  and forms a crystalline *methiodide* which decomposes at  $153$ — $154^\circ$ . The decomposition of the base by acetic anhydride yields the same basic products as the monochloro-compound, and 3-methoxy-4:9-(or 4:10)-diacetoxyphenanthrene. The latter substance, which has been obtained by Knorr by the degradation of hydroxycodine, has its constitution partially determined by its oxidation to 4-acetoxy-3-methoxyphenanthraquinone.

*Benzoylcodeine methiodide*,  $C_{26}H_{28}O_4NI$ , melts at  $254^\circ$  (corr.). *Benzoyl- $\alpha$ -methylmorphimethine* melts at  $182$ — $183^\circ$ , and its *methiodide*,



at  $188^\circ$ . Codeine yields with phenylcarbimide the *anilincarboxylic ester*, which melts at  $141^\circ$ ; the *methiodide*,  $C_{26}H_{29}O_4N_2I$ , at  $141^\circ$ . The corresponding compound of  $\alpha$ -methylmorphimethine melts at  $122$ — $123^\circ$ , and its *methiodide* at  $251^\circ$  (corr.). C. S.

**Constitution of apoMorphine.** ROBERT PSCHORR [and WALTHER KARO] (*Ber.*, 1906, 39, 3124—3128. Compare Abstr., 1903, i, 193).—The methylation of *apomorphine* by methyl sulphate instead of by diazomethane leads to the ultimate formation of dimethoxyvinylphenanthrene in quantitative yield. When the latter is oxidised rapidly in acetone by potassium permanganate, there is formed, in addition to the acid described previously (*loc. cit.*), *dimethoxyphenanthrylglycol*,



which forms glistening leaflets and melts at  $145^\circ$  (corr.); the *acetate*,  $C_{22}H_{22}O_6$ , melts at  $126$ — $127^\circ$  (corr.).

*Pentabromodimethoxyvinylphenanthrene*,  $C_{18}H_{13}O_2Br_5$ , resulting by

the bromination of the tribromo-compound (*loc. cit.*), melts at 153—154° (corr.).

By distillation with zinc dust, dimethylapomorphimethine or dimethoxyvinylphenanthrene yields two *ethylphenanthrenes*,  $\alpha$  and  $\beta$ . The former is volatile with steam, melts at 109—110°, and forms a *picrate*,  $C_{16}H_{14}C_6H_3O_7N_3$ , which melts at 138—140° (corr.), and a *quinone* which melts at 187—188° (corr.).

The  $\beta$ -compound crystallises in needles and melts at 172—173° (corr.). The nitrogenous products of the distillation are hydrogen cyanide, ammonia, and trimethylamine.  
C. S.

**Narceine. I. Alkylnarceines and Alkylhomonarceines.**  
RUDOLPH TAMBACH and CARL JAEGER (*Annalen*, 1906, 349, 185—200. Compare Freund and Frankforter, *Abstr.*, 1894, i, 58).—The sodium salt of narceine melts at 163—165°.

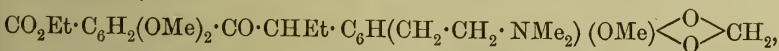
When boiled together in absolute alcoholic solution, narceine and methyl sulphate form an additive compound, which crystallises from alcohol in rhomboids or from water in slender needles, and melts at 200—201°.

*Methylnarceine,*



is formed by treating narceine with the calculated amounts of *N*-sodium hydroxide and methyl sulphate; it melts and decomposes at 266°; the *hydrochloride*,  $C_{24}H_{29}O_8N, HCl$ , crystallises from alcohol and melts at 243°; the *sodium* derivative crystallises in nacreous, glistening leaflets and is readily soluble in water or alcohol; the *platinichloride* forms yellow leaflets and melts at 209—210°.

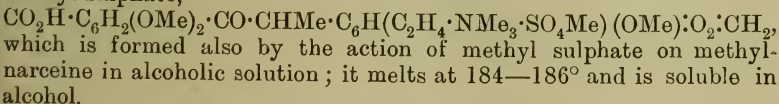
*Ethylnarceine*, prepared by the action of ethyl sulphate on narceine in sodium hydroxide solution, melts at 175—177°; the *hydrochloride*,  $C_{25}H_{31}O_8N, HCl$ , melts at 231°; the *platinichloride* melts at 174°. When heated with alcoholic hydrogen chloride, the base forms *ethyl narceine*,



which is isolated as the *hydrochloride*,  $C_{27}H_{35}O_8N, HCl$ , melting at 218.5—219°; the *platinichloride* melts at 220°.

The alkylnarceines may be prepared by the action of alkyl haloids instead of the alkyl sulphates on narceine in alcoholic sodium or potassium hydroxide instead of *N*-sodium hydroxide solution or on sodium narceine.

The alkali salts of narceine react with 2 mols. of methyl sulphate in alcoholic solution, forming an *additive* compound of methylnarceine and methyl sulphate,



The authors have repeated part of Freund's experiments (*loc. cit.*). The action of methyl iodide on narceine in boiling ethyl-alcoholic

potassium hydroxide, or on sodium narceine in boiling methyl or ethyl alcohol, or on methylnarceine at 110—120°, leads to the formation of methylnarceinium methiodide melting at 207—209°. The action of ethyl iodide on sodium narceine in boiling ethyl-alcoholic solution or in the absence of a solvent, leads to the formation of ethyl-narceinium ethiodide; methylnarceine was not obtained by the action of methyl alcohol on sodium narceine. The alcohol takes no part in the reaction.

*Ethylnarceinium methiodide*, formed by heating ethylnarceine with methyl iodide, melts at 209—211° or, when mixed with methyl narceinium methiodide, at 200°. *Ethyl narceinium ethiodide*, prepared from ethylnarceine and ethyl iodide, crystallises in sheaves of large needles, melts at 191—193°, and forms a yellow precipitate when treated with sodium hydroxide in aqueous solution.

Methylhomonarceine, prepared by treating homonarceine with methyl sulphate and sodium hydroxide, is isolated as the *hydrochloride*, which crystallises in sheaves of prisms and melts and decomposes at 230—231°; the *platinichloride* melts at 181—182°.

*Ethyl methylhomonarceine hydrochloride*, prepared by boiling the preceding substance with alcoholic hydrogen chloride, melts at 212°, and gives an intense yellow coloration with aqueous sodium hydroxide; the *platinichloride* melts at 217—218°.

*Ethylhomonarceine*, prepared from homonarceine, ethyl sulphate, and *N*-sodium hydroxide, is isolated as the *hydrochloride*, melting and decomposing at 212°; the *platinichloride* melts at 152—155°.

*apoN*Narceine,



is prepared by heating narceine with phosphorus oxychloride; it crystallises from alcohol, melts at 112—115°, is readily soluble in hot alcohol, but only sparingly so in water, and is insoluble in aqueous alkali hydroxides. The *hydrochloride*,  $\text{C}_{23}\text{H}_{25}\text{O}_7\text{N}, \text{HCl}, \text{H}_2\text{O}$ , is an intense canary-yellow, melts at 144°, and is hydrolysed by boiling aqueous sodium hydroxide.

G. Y.

**Constitution of Histidine.** ADOLF WINDAUS and FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1906, 8, 406—408. Compare Abstr., 1905, i, 834).—According to Niementowski (*Ber.*, 1899, 32, 1460; compare O. Fischer, Abstr., 1901, i, 413), the rupture of an iminazole ring by the action of benzoyl chloride is by no means general, and hence Fränkel's criticism (this vol., i, 547) of the authors' iminazole formula for histidine has little value.

Potassium hydroxide and benzenesulphonic chloride, or naphthalene sulphonic chloride, do not rupture the ring in methyliminazole. The histidinecarboxylic acid described by Fränkel melts at 209° (corr.), and not at 195°, and is identical with the glyoxaline-4-carboxylic acid previously described by the authors.

J. J. S.

**Erlenmeyer, jun.'s, Brucine Cinnamates.** WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, 39, 2598—2600. Compare Erlenmeyer, jun., Abstr., 1905, i, 892; this vol., i, 21, 176; Erlen-



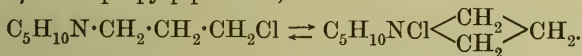
meyer, jun., and Barkow, this vol., i, 429; Marckwald and Meth, this vol., i, 360, 585).—The authors consider that Erlenmeyer, jun.'s, conclusions regarding the stereoisomeric cinnamic acids are erroneous. The optically inactive salt, described by Erlenmeyer as having been obtained from naturally occurring cinnamic acid and brucine, and sometimes also from the synthetical acid and brucine, is obtained by the authors by the combination of cinnamic acid (2 mols.) and brucine (1 mol.). The salt  $C_{23}H_{26}O_4N_2(C_9H_8O_2)_2$  melts at  $135^\circ$ , as Erlenmeyer found, but is not quite inactive, a 1 per cent. solution of it giving  $\alpha_D - 5'$  in a 2-dcm. tube.

A. McK.

**Preparation of Sodium Theobromine Formate.** F. HOFFMANN, LA ROCHE & CIE. (D.R.-P., 172932).—The double salt, *sodium theobromine formate*,  $NaC_7H_7O_2N_4 \cdot HCO_2Na \cdot H_2O$ , is prepared by mixing aqueous solutions containing molecular proportions of pure sodium theobromine and anhydrous sodium formate; the solution is evaporated to dryness on the water-bath, when the product is obtained as a white powder of bitter taste. This substance is employed therapeutically, and has a powerful diuretic action.

G. T. M.

**Tertiary and Quaternary Bases from Piperidine.** SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1906, 39, 2875—2888. Compare Gabriel and Stelzner, *Abstr.*, 1896, i, 702; Hörlein and Kneisel, this vol., i, 458).— $\gamma$ -Chloropropylpiperidine is transformed into a quaternary salt when evaporated with water, but if the heating is continued in order to drive off all the water, the quaternary salt is transformed back into  $\gamma$ -chloropropylpiperidine,



When the pure quaternary salt is distilled with 50 per cent. potassium hydroxide solution until the distillate is no longer alkaline, the chief product is a *base*,  $C_{16}H_{32}ON_2$ , distilling at  $336-339^\circ$ . No neutral products and no piperidine, allylpiperidine, or trimethylenedipiperidine appear to be formed. These products could not be isolated when the crude chloride containing unaltered  $\gamma$ -chloropropylpiperidine was used.

The base  $C_{16}H_{32}ON_2$  yields an *aurichloride* melting at  $131-132^\circ$ , a *platinichloride*,  $C_{16}H_{34}ON_2PtCl_6$ , which sinters at  $220^\circ$ , and melts and decomposes at  $223-224^\circ$ , a *picrate* melting at  $150-151^\circ$ , a *hydrochloride* in the form of a crystalline, hygroscopic powder melting at  $220-221^\circ$ , and a *hydriodide* in colourless rhombs melting at  $135-136^\circ$ . The same base is obtained when trimethylenepiperylum hydroxide is heated with water at  $50^\circ$ ; it is represented as *dipiperidinodipropyl ether*,  $O(CH_2 \cdot CH_2 \cdot CH_2 \cdot NC_5H_{10})_2$ .

The base reacts with methyl iodide, yielding a *dimethiodide*,



which melts at  $165-168^\circ$  after sintering at  $140^\circ$ . The corresponding *platinichloride*,  $C_{18}H_{38}ON_2PtCl_6$ , melts and decomposes at  $244^\circ$ , and the *aurichloride* melts at  $164-165^\circ$  after sintering at  $155^\circ$ . When heated with hydrochloric acid at  $150^\circ$ , the base yields  $\gamma$ -chloropropylpiperidine hydrochloride, and when boiled with hydriodic acid

$\gamma$ -iodopropylpiperidine hydriodide. The *picrate* of  $\gamma$ -iodopropylpiperidine sinters at  $95^{\circ}$  and melts at  $99$ — $100^{\circ}$ .

$\gamma$ -Methoxypropylpiperidine,  $C_5H_{10}N \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OMe$ , obtained by the action of  $\alpha$ -chloropropyl methyl ether on piperidine, is an oil distilling at  $199$ — $203^{\circ}$  under 766 mm. pressure. It dissolves readily in water, and the solution has a distinctly alkaline reaction. The *aurichloride* crystallises in golden-yellow, hexagonal plates, melting at  $68$ — $69^{\circ}$ . When boiled for a short time with hydriodic acid, the base yields  $\gamma$ -iodopropylpiperidine hydriodide.

Trimethylenedipiperidine and trimethylene bromide were condensed in the hope of obtaining the bromide of the octocyclic base described by Hörlein and Kneisel, but without result. J. J. S.

**Reduction of *o-p*-Dinitrophenylpiperidine.** LEOPOLD SPIEGEL and A. UTERMANN (*Ber.*, 1906, 39, 2631—2638).—Since substances of the aminophenylpiperidine class are of pharmacological interest, the authors describe several new compounds prepared from *o-p*-dinitrophenylpiperidine by a modification of Lellmann and Geller's method (*Abstr.*, 1888, 1107). Whilst Lellmann and Geller obtained from the dinitro-compound in question substances containing chlorine, the authors by variation of the conditions obtain *o-p*-diaminophenylpiperidine and also *o*-amino-*p*-nitrophenylpiperidine. The position of the nitro-group in the latter substance was determined by transformation into *p*-nitrophenylpiperidine by means of the diazo-reaction. By the reduction of the dinitro-compound in alcoholic solution with ammonium sulphide, a small amount of *p*-amino-*o*-nitrophenylpiperidine was also obtained.

*o-p*-Dinitrophenylpiperidine was prepared by adding piperidine (2 mols.) to an alkaline solution of chloro-2:4-dinitrobenzene, keeping the temperature below  $45^{\circ}$ , and then boiling until the solution was complete.

*o-p*-Diaminophenylpiperidine,  $C_5H_{10}N \cdot C_6H_3(NH_2)_2$ , prepared by the reduction of *o-p*-dinitrophenylpiperidine by stannous chloride, separates from light petroleum in prisms and melts at  $76^{\circ}$ . Its *hydrochloride* forms transparent needles and melts indefinitely at  $225^{\circ}$ .

*Diacetyl-o-p*-diaminophenylpiperidine *hydrochloride* separates from a mixture of alcohol and ether in needles and melts at  $245^{\circ}$ . *Diacetyl-o-p*-diaminophenylpiperidine separates from alcohol or light petroleum in grey leaflets and melts at  $183^{\circ}$ .

*Piperidino-m-phenylenediurethane*,  $C_5H_{10}N \cdot C_6H_3(NH \cdot CO_2Et)_2$ , prepared by the addition of ethyl chlorocarbonate to an ethereal solution of *o-p*-diaminophenylpiperidine, separates from a mixture of acetone and light petroleum in transparent, rhombic plates.

*Piperidino m-phenylenedicarbamide*,  $C_5H_{10}N \cdot C_6H_3(NH \cdot CO \cdot NH_2)_2$ , prepared from potassium isocyanate and *o-p*-diaminophenylpiperidine *hydrochloride*, separates from a mixture of acetone and light petroleum in stellate needles and melts at  $190^{\circ}$ .

*p*-Nitro *o*-aminophenylpiperidine,  $C_5H_{10}N \cdot C_6H_3(NO_2) \cdot NH_2$ , prepared by the partial reduction of *o-p*-dinitrophenylpiperidine by ammonium sulphide or by stannous chloride, separates from light petroleum in prisms or pyramids and melts at  $86^{\circ}$ . Its *hydrochloride* is unstable.

4-Nitro-2-acetylaminophenylpiperidine,  $C_5H_{10}N \cdot C_6H_3(NO_2) \cdot NHAc$ , separates from light petroleum in yellow prisms and melts at  $106^\circ$ .

Piperidino-4-nitrophenyl-2-urethane,  $C_5H_{10}N \cdot C_6H_3(NO_2) \cdot NH \cdot CO_2Et$ , separates from a mixture of acetone and water in pale yellow needles and melts at  $120^\circ$ .

Dipiperidino-4-nitrophenyl-2-carbamide,  $CO[NH \cdot C_6H_3(NO_2) \cdot C_5H_{10}N]_2$ , prepared by the addition of a solution of phosgene in toluene to a solution of 4-nitro-2-aminophenylpiperidine in benzene, separates from a mixture of acetone and light petroleum in needles and melts at  $206^\circ$ .

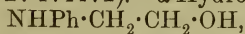
2-Nitro-4-aminophenylpiperidine,  $C_5H_{10}N \cdot C_6H_3(NO_2) \cdot NH_2$ , formed, together with its isomeride, by the reduction of 2:4-dinitrophenylpiperidine with ammonium sulphide, separates from light petroleum in dark red needles and melts at  $112.5^\circ$ .  
A. McK.

*iso*Propyl-4-stilbazole, *m*-Methyl-4-stilbazole, and *m*-Methyl-2-stilbazole. HERMANN FREUND (*Ber.*, 1906, 39, 2833—2837).—*iso*Propyl-4-stilbazole, prepared by heating 4-picoline with cuminaldehyde in presence of zinc chloride, melts at  $65-67^\circ$  and forms a golden-yellow, crystalline *picrate* melting at  $188-190^\circ$ , a yellowish-white *mercurichloride* melting at  $165-167^\circ$ , and a yellow *platinichloride* melting at  $191-193^\circ$ . The *dibromide* forms reddish-yellow crystals, which sinter at  $135^\circ$  and melt at  $144-146^\circ$ . *iso*Propyl-dihydro-4-stilbazole is a yellow oil boiling at  $185-195^\circ$  under 35 mm. pressure; the *aurichloride* melts at  $116-117^\circ$ .

*m*-Methyl-4-stilbazole is a colourless oil distilling between  $220^\circ$  and  $225^\circ$  under 35 mm. pressure; the *picrate* forms yellow crystals, melting at  $194-196^\circ$ ; the *aurichloride* sinters at  $158^\circ$  and melts at  $166-168^\circ$ ; the *platinichloride* melts between  $194^\circ$  and  $195^\circ$ , and the *dibromide* at  $125-127^\circ$ . *m*-Methyldihydro-4-stilbazole is a colourless liquid, boiling at  $220^\circ$  under 60 mm. pressure; the *picrate* melts at  $122-124^\circ$ , the *platinichloride* at  $171-172^\circ$ . *m*-Methyl-4-stilbazoline is a viscous, reddish-yellow oil, distilling at  $200^\circ$  under 50 mm. pressure.

*m*-Methyl-2-stilbazole is a light, mobile oil, boiling at  $220^\circ$  under 45 mm. pressure; the *picrate* melts at  $214-215^\circ$ ; the *aurichloride* forms needles melting at  $135-136^\circ$ ; the *platinichloride* melts at  $186-187^\circ$ ; the *dibromide* melts at  $145-146^\circ$ . *m*-Methyldihydro-2-stilbazole is a colourless oil, boiling at  $220^\circ$  under 35 mm. pressure; the *picrate* melts at  $131-132^\circ$ , the *aurichloride* at  $79-80^\circ$ , and the *platinichloride* at  $156-157^\circ$ . *m*-Methyl-2-stilbazoline is a light oil, distilling at  $195-197^\circ$  under 35 mm. pressure.  
E. F. A.

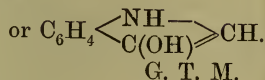
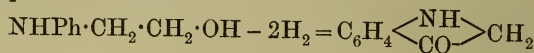
Preparation of Indoxyl and its Derivatives. BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 171172).— $\alpha$ -Hydroxyethylaniline,



its homologues, alkali derivatives, carboxylic acids, or the *N*-alkyl derivatives of the foregoing substances when fused with alkali metals, alkali amides, alkali hydroxides, or mixtures of these with the oxides



of the alkaline earth metals, furnish indoxyl and indigotin on appropriate treatment :



**A New Indolenine Base.** DUŠAN J. GRGIN (*Monatsh.*, 1906, 27, 731—742. Compare Plancher, *Abstr.*, 1898, i, 536 ; Brunner, *Abstr.*, 1900, i, 360).—*p*-Tolylhydrazine reacts with isobutaldehyde at 60°, forming water and 3:3:5-trimethylindolenine, which is isolated as the zincchloride,  $(\text{C}_{11}\text{H}_{13}\text{N})_2\text{ZnCl}_2$ ; this crystallises from alcohol in almost

white leaflets and melts at 208—209°. The base,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{CH}$ ,

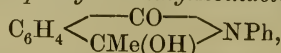
boils at 198—200° under 30 mm. pressure, crystallises with difficulty in almost colourless leaflets, melts at 142—143°, or, in consequence of polymerisation, after four and a half days in a vacuum at 156—157°, or after twenty days at 172—173°. The base melting at 172—173° forms with silver nitrate a precipitate,  $(\text{C}_{11}\text{H}_{13}\text{N})_2\text{C}_{11}\text{H}_{12}\text{NAg}$ , which is sensitive to light; the base melting at 142—143° does not form a precipitate with silver nitrate. The picrate,  $\text{C}_{11}\text{H}_{13}\text{N} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_2$ , crystallises in glistening, yellow prisms and melts at 169—170°; the platinichloride,  $(\text{C}_{11}\text{H}_{13}\text{N})_2\text{H}_2\text{PtCl}_6$ , crystallises in dark yellow prisms.

When heated with concentrated hydrochloric acid in a reflux apparatus, the indolenine base is converted into 2:3:5-trimethyl indole, which melts at 190° and forms a picrate melting at 177—180° (compare Wolff, *Abstr.*, 1889, 259).

Digestion of the indolenine base with ammoniacal silver nitrate on the water-bath leads to the formation of the corresponding indolinone, which is obtained as a white, crystalline substance, becoming brown on drying, and melting at 146°.

The action of bromine on the indolenine base in hydrochloric acid solution leads to the formation of the derivative,  $\text{C}_{11}\text{H}_{12}\text{ONBr}$ , which crystallises in light yellow leaflets and melts at 203—204°. G. Y.

**Action of Mixed Organomagnesium Compounds on Imides.** CONSTANTIN BÉIS (*Compt. rend.*, 1906, 143, 430—432. Compare *Abstr.*, 1904, i, 503, 671 ; Sachs and Ludwig, *Abstr.*, 1904, i, 266).—Phenylphthalimide reacts with nascent magnesium alkyl halides to form substituted isoindolinones, and the following compounds were thus prepared. 3-Hydroxy-2-phenyl-3-methylisoindolinone,



forms colourless crystals melting at 185°, and 3-hydroxy-2-phenyl-3-ethylisoindolinone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CEt(OH)} \end{array} \text{NPh}$ , colourless crystals melting

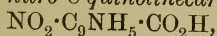
at 160°. With nascent magnesium phenyl bromide, phenylphthalimide yields a mixture of 3-hydroxy-2:3-diphenylisoindolinone, melting at 195°, and benzoylbenzophenone,  $\text{C}_6\text{H}_4(\text{COPh})_2$ , melting at 149° (compare Zincke, this Journal, 1876, i, 703), separated by their difference of solubility in benzene and in alcohol.

M. A. W.

**Halogen Derivatives of 8-Methylquinoline and Nitro-8-quinolinealdehyde.** JOH. HOWITZ and PAUL NÖTHER (*Ber.*, 1906, 39, 2705—2713. Compare *Abstr.*, 1902, i, 397; 1905, i, 471).—The compounds described previously as 8-bromomethylquinoline and 3-bromo-8-bromomethylquinoline are in reality 8-chloromethylquinoline and 3-bromo-8-chloromethylquinoline respectively, since in the course of their preparation hydrochloric acid is employed, whereby the bromine in the side-chain is replaced almost entirely by chlorine. Pure 8-chloromethylquinoline crystallises in large, glistening plates and melts at 56°.

When the product obtained under Lang's conditions (*Diss.*, Freiburg, 1898) is dissolved in a mixture of equal volumes of concentrated sulphuric acid and water, and the solution poured into a large volume of water, 3-bromo-8-bromomethylquinoline is precipitated, whilst from the filtrate sodium hydroxide precipitates 8-bromomethylquinoline. The former,  $C_9NH_5Br \cdot CH_2Br$ , separates from alcohol in colourless leaflets and melts at 145°. The latter,  $C_9NH_6 \cdot CH_2Br$ , separates from light petroleum in long, colourless needles or prisms, melts at 84°, and forms a *hydrobromide*,  $C_9NH_6 \cdot CH_2Br \cdot HBr$ , which darkens at 250°, but does not melt at 320°. By nitration it yields 5-nitro-8-bromomethylquinoline,  $NO_2 \cdot C_9NH_5 \cdot CH_2Br$ , which forms yellow needles or prisms and melts at 116°.

5-Nitro-8-iodomethylquinoline,  $NO_2 \cdot C_9NH_5 \cdot CH_2I$ , obtained from the corresponding chloro-compound and potassium iodide in aqueous-alcoholic solution, forms yellow needles and melts at 142°. By oxidation with dilute nitric acid (1:1), a quantitative yield of 5-nitro-8-quinolinealdehyde,  $NO_2 \cdot C_9NH_5 \cdot CHO$ , is obtained, which separates from hot water in slender, white needles, melts at 146—147°, reduces ammoniacal silver solutions, and is oxidised by chromic acid in warm dilute sulphuric acid to 5-nitro-8-quinolinecarboxylic acid,



which melts at 212°.

C. S.

[Action of Alkyl Sulphates and Sulphonates on Quinoline Bases.] FÄRBEFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 170048, 170049).—The colouring matters produced by the interaction of alkylsulphonates and quinoline bases, and subsequent treatment with alkali hydroxides, are valuable sensitising compounds which are readily prepared and have favourable absorption spectra.

Quinaldine and ethyl ethanesulphonate combine additively to form an oily product which on treatment with alcoholic potash furnishes a colouring matter crystallising from ether or alcohol in green bronzy needles, and dissolving in water to a red solution.

The additive product,  $C_{10}NH_9Et \cdot SO_3Ph$ , of quinaldine and ethyl benzenesulphonate was obtained crystalline and melted at 105°; when treated with warm alcoholic potash it furnished a colouring matter separating in bright golden-bronzy leaflets. A similar compound was produced from quinaldine and ethyl *p*-bromotoluenesulphonate. The additive compounds obtained from ethyl *p*-toluenesulphonate and 2:6-dimethylquinoline and quinaldine melted at 120° and 134° respectively;

that from this ester and 6-bromoquinoline was oily, but all gave colouring matters on treatment with alcoholic potash.

2:7- and 2:6-Dimethylquinolines combine additively with methyl sulphate, and in the latter case a crystalline product melting at  $212^{\circ}$  was obtained. On treatment with alcoholic potash, crystalline colouring matters are produced, the compound from the 2:7-base having a steel-blue lustre, whilst that from the 2:6-isomeride separates in lustrous, dark green needles.

G. T. M.

**Colouring Matters of the Quinolinium Series.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172118).—By the action of alkalis on the alkyl halides of quinaldine bases, or mixtures of these salts of the quinaldine and quinoline bases, red colouring matters are produced which have been employed as sensitisers in photographic practice. It is now found that quite different products are obtained when the alkali acts on these bases in the presence either of formaldehyde or of substances yielding this aldehyde. A colouring matter dissolving readily in the organic solvents, and sparingly in water to intense blue solutions, is produced on treating an alcoholic solution of quinoline and quinaldine hydriodides with sodium hydroxide and formaldehyde. The new compound separates in well-defined crystals having a green metallic reflex; it can be recrystallised from boiling methyl alcohol. Similar colouring matters are obtained from the methochlorides of quinoline and quinaldine, and the reaction takes place also in aqueous or pyridine solutions.

G. T. M.

**Dyeing Properties of the Condensation Products of Quinaldine with Aldehydes.** EMILIO NOELTING and E. WITTE (*Ber.*, 1906, 39, 2749—2751).—Benzylidenequinaldine [2-styrylquinoline] (*Abstr.*, 1884, 336) itself is a dye, and a 3 per cent. solution of the hydrochloride yields an intense yellow colour with cotton mordanted with tannic acid. The *p*-nitro-derivative (Bulach, *Abstr.*, 1887, 976) gives a somewhat more greenish shade. The isomeric *o*- and *m*-nitro-compounds, piperonylidene- and nitropiperonylidene-quinaldine, give yellow shades. Dihydroxybenzylidenequinaldine (Nencki, *Abstr.*, 1894, i, 520), in the form of its hydrochloride, dyes wool, silk, or cotton mordanted with tannic acid orange-red. The *diacetyl* derivative, which melts at  $165^{\circ}$ , gives a yellow shade.

*p*-Dimethylaminobenzylidenequinaldine,  $C_{19}H_{18}N_2$ , crystallises from alcohol in pale yellow plates, or from benzene in brownish-yellow, flat needles melting at  $177^{\circ}$ . The *platinichloride* and *picrate* have been prepared.

*p*-Aminobenzylidenequinaldine melts at  $154^{\circ}$ , and its *hydrochloride* forms pale red needles, which become deep red when dry and melt at  $273^{\circ}$ . It dyes cotton mordanted with tannic acid a brilliant red.

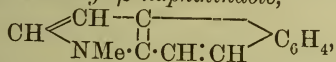
J. J. S.

**Preparation and Hydrogenation of 1-Methyl- $\beta$ -naphthindole.** ROBERT PSCHORR and WALTHER KARO (*Ber.*, 1906, 39, 3140—3144).— $\beta$ -Naphthylmethylaniline is obtained conveniently by the methylation



of acet- $\beta$ -naphthalide or of the benzenesulphonamide, followed by hydrolysis of the product. The *hydrochloride* melts at  $182-183^\circ$  (corr.), the *picrate* at  $145^\circ$  (corr.), and the *phenylcarbamide* at  $133-134^\circ$  (corr.).

Sodium 1-methyl- $\beta$ -naphthindolesulphonate,  $C_{13}H_{10}N \cdot SO_3Na$ , obtained by Hinsberg's method (Abstr., 1895, i, 144), melts at  $169^\circ$  (corr.), and by hydrolysis yields 1-methyl- $\beta$ -naphthindole,



which melts at  $53^\circ$  and forms a red *picrate* melting at  $172-173^\circ$  (corr.). By reduction of an alcoholic solution of the naphthindole by zinc and hydrogen chloride, 1-methyldihydro- $\beta$ -naphthindole is obtained quantitatively; it melts at  $40-41^\circ$ . The *hydrochloride* melts at  $205-206^\circ$  (corr.), the *picrate* at  $158^\circ$  (corr.), the *methiodide* at  $220-221^\circ$  (corr.). The dihydrogenated base is converted by sodium and amyl alcohol into the *ar*-tetrahydro-compound,  $C_{13}H_{17}N$ , which boils at  $160-180^\circ$  under 14 mm. pressure, and does not form a carbonate. The *hydrochloride* melts at  $186-187^\circ$  (corr.), the *picrate* at  $169^\circ$  (corr.), the *methiodide* at  $236-237^\circ$  (corr.). The tertiary base is regenerated from the *picrate* by alcoholic potash at  $160^\circ$ .

C. S.

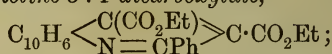
**Synthesis in the Acridine Series.** CARLO BAEZNER and AUGUST GARDIOL (*Ber.*, 1906, 39, 2623—2625. Compare Abstr., 1904, i, 928; this vol., i, 699, 901).—The condensation product from aniline and *o*-nitrobenzyl chloride undergoes a change similar to that of *o*-nitrobenzyl chloride itself, which, when reduced by stannous chloride in the presence of primary or secondary amines and  $\beta$ -naphthol, yields acridine derivatives.

When *o*-nitrobenzyl chloride and aniline are warmed together, the main product is *o*-nitrobenzylaniline, whilst phenyl *o*-dinitrobenzylamine is also produced. When *o*-nitrobenzylaniline is reduced in alcoholic solution with aluminium amalgam, it forms *o*-aminobenzylaniline,  $NHPh \cdot CH_2 \cdot C_6H_4 \cdot NH_2$ , which crystallises from a mixture of water and alcohol in tiny needles and melts at  $81^\circ$ . When condensed with  $\beta$ -naphthol, it forms 1:2-phenonaphthacridine, melting at  $132^\circ$ , and identical with the product which Ullmann and Baezner (Abstr., 1902, i, 694) had previously obtained from *o*-aminobenzyl alcohol and  $\beta$ -naphthol.

In an analogous manner, 7-hydroxy-1:2-phenonaphthacridine, previously obtained by Baezner (Abstr., 1904, i, 928), may be prepared from *o*-aminobenzylaniline and 2:7-dihydroxynaphthalene. A characteristic reaction of this compound is the behaviour of its methiodide towards ammonia when the compound  $C_{18}H_{13}ON$  is formed; the latter is dark blue, is insoluble in alkali, and melts at  $227^\circ$ . A. McK.

**Syntheses in the Quinoline Group; Phenyl-naphthaquinoline-dicarboxylic Acid and its Derivatives.** LOUIS J. SIMON and CH. MAUGUIN (*Compt. rend.*, 1906, 143, 427—430).—The compound

$C_{25}H_{21}O_4N$ , prepared by oxidising the cyclic compound obtained by the elimination of  $H_2O$  from the condensation product of ethyl oxalacetate and benzylidene  $\beta$ -naphthylamine (Abstr., 1904, i, 812), is *ethyl-2-phenyl- $\beta$ -naphthaquinoline-3:4-dicarboxylate*,



it melts at  $128^\circ$ , can be distilled under reduced pressure at  $305^\circ$ , and is not changed by warming with concentrated hydrochloric or sulphuric acid or potassium hydroxide solution. The *acid*,  $C_{19}H_{11}N(\text{CO}_2\text{H})_2$ , obtained from the ester by prolonged heating (fifteen hours) with a 15 per cent. alcoholic solution of potassium hydroxide, forms pale yellow, microscopic needles insoluble in water or the ordinary solvents. It can be titrated in the presence of phenolphthalein, yielding the alkali salt from which the *silver*, *copper*, *lead*, *calcium*, and *barium* salts have been prepared by double decomposition. The *copper ammonium* salt,  $C_{19}H_{11}N \begin{array}{c} \text{CO}_2 \\ \text{CO}_2 \end{array} \gg \text{Cu}, 3\text{NH}_3, 6\text{H}_2\text{O}$ , forms deep blue, brilliant prisms.

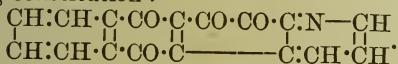
The *anhydride*,  $C_{19}H_{11}N \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \gg \text{O}$ , obtained by fusing the acid at  $218^\circ$ , crystallises from boiling acetic acid or anhydride in golden yellow needles which melt at  $218^\circ$ , and yields the potassium salt of the acid by the action of aqueous or alcoholic potassium hydroxide, and the *ethyl hydrogen ester*,  $\text{CO}_2\text{H} \cdot C_9H_{11}N \cdot \text{CO}_2\text{Et}, \text{EtOH}$ , on boiling with absolute alcohol. The same ester is also obtained when the diethyl ester is heated for five hours with a 2 per cent. alcoholic solution of potassium hydroxide; it forms massive, rhombic, highly refractive crystals of an amber-yellow colour, loses its alcohol of crystallisation at  $115^\circ$ , and crystallises from methyl alcohol in long, white, silky needles containing 1 mol. of methyl alcohol of crystallisation. 2-Phenyl- $\beta$ -naphthaquinoline (compare Döbner and Kuntze, Abstr., 1889, 411, 412) is obtained by heating 2-phenyl- $\beta$ -naphthaquinoline-3:4-dicarboxylic acid or any of its derivatives with soda lime.

M. A. W.

**Syntheses in the Quinoline Group; Ethyldihydrophenyl-naphthaquinolinedicarboxylate and its Derivatives.** LOUIS J. SIMON and CHARLES MAUGUIN (*Compt. rend.*, 1906, 143, 466—468. Compare preceding abstract).—The yellow compound,  $C_{25}H_{23}O_4N$ , melting at  $146$ — $147^\circ$ , obtained by the elimination of  $H_2O$  from the condensation product of ethyl oxalacetate, benzaldehyde, and  $\beta$ -naphthylamine (Abstr., 1904, i, 812), is probably ethyl dihydrophenylnaphthaquinolinedicarboxylate; it is not attacked by hot concentrated aqueous potassium hydroxide, but is decomposed by fusing with potassium hydroxide, yielding a mixture of 2-phenylnaphthaquinoline,  $C_{19}H_{13}N$ , and 2-phenylnaphthaquinoline-4-carboxylic acid,  $C_{19}H_{12}N \cdot \text{CO}_2\text{H}$ , identical with the compounds prepared by Döbner (Abstr., 1889, 411, 412). 2-Phenylnaphthaquinoline trichloroacetate,  $C_{19}H_{13}N_3, 2(\text{CCl}_3 \cdot \text{CO}_2\text{H})$ , is a characteristic salt, and the *copper ammonium* salt of 2-phenylnaphthaquinoline-4-carboxylic acid crystallises in small, blue prisms, and the *methyl ester* of the acid obtained by the action of methyl sulphate melts at  $128^\circ$  and is not changed by boiling with concentrated potassium hydroxide.

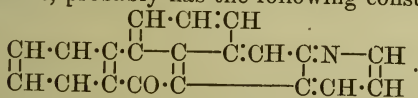
M. A. W.

**Preparation of an Oxidation Product of Alizarin-blue.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 171836).—Energetic oxidation of alizarin-blue leads to the disruption of the anthraquinone nucleus and the formation of phthalic acid. When alizarin-blue in solution, or suspension in water, is treated with mild oxidising agents either in neutral or acid solution it becomes converted into a yellow *compound* of quinonoid character, which in all probability has the following constitution :



This substance, which is called *alizarin-blue-quinone*, is reconverted into alizarin-blue by mild reducing agents, whilst treatment with ammonia transforms it into *alizarin-blue-amide*. Chlorine, bromine, hypochlorites, manganese dioxide, lead peroxide, and dilute nitric acid may be employed as oxidising agents, but when the last of these is used the product is a salt-like compound of the ortho-quinone and the acid which evolves nitrous fumes on warming with glacial acetic acid, whilst pure alizarin-blue quinone itself separates in well-defined crystals on cooling the solution or on adding alcohol. G. T. M.

**Preparation of Benzanthronequinolines.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 171939).—Although  $\beta$ -aminoalizarin when condensed with glycerol yields alizarin-blue, the quinoline of alizarin, yet this condensation when applied to  $\beta$ -aminoanthraquinone results in the formation of substances containing two new rings,  $\text{C}_{14}\text{H}_9\text{O}_2\text{N} + 2\text{C}_3\text{H}_8\text{O}_3 = \text{C}_{20}\text{H}_{11}\text{ON} + 7\text{H}_2\text{O}$ . The principal product, which is called *benzanthronequinoline*, probably has the following constitution :



When crystallised from toluene this substance separates in well-defined yellow needles melting at  $251^\circ$ . Another product of this condensation which melts at  $232\text{--}234^\circ$  is not homogeneous, because by fractional crystallisation it may be resolved into benzanthronequinoline, and another substance,  $\text{C}_{17}\text{H}_9\text{O}_2\text{N}$ , which melts at  $322^\circ$  and is isomeric with Graebe's anthraquinonequinoline.

Similar condensation products may be obtained from 2:6- and 2:7-diaminoanthraquinones and the sulphonic acids of the mono- and di-aminoanthraquinones. G. T. M.

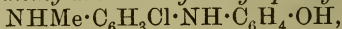
**Supposed Penthiazole Derivatives.** SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1906, 39, 2889—2892. Compare Gadamer, *Abstr.*, 1896, i, 415; Gabriel and Hoisch, *ibid.*, 1897, i, 136).—Dixon's bromoethoxypenthiazoline (*Trans.*, 1896, 69, 31) is regarded

as ethoxybromomethylthiazoline,  $\text{CH}_2\text{Br} \cdot \text{CH} - \text{S} \begin{array}{l} | \\ \text{CH}_2 \cdot \text{N} \end{array} \gg \text{C} \cdot \text{OEt}$ , since when oxidised with bromine water it yields *bromomethyltaurine*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{Br}) \cdot \text{SO}_3\text{H}$ , which crystallises from water in rectangular plates melting and



decomposing at  $273^{\circ}$ . When reduced with zinc and sulphuric acid, the bromo-derivative yields  $\beta$ -methyltaurine. Bromomethyltaurine yields a *potassium* salt,  $C_3H_7O_3NSBrK$ , in the form of colourless, glistening plates, it dissolves readily in water, and when the solution is heated potassium bromide and *trimethyleneiminesulphonic acid*,  $NH\langle\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}\rangle CH\cdot SO_3H$ , are formed. The latter sinters at  $230^{\circ}$ , melts at about  $245$ — $247^{\circ}$  and decomposes at  $255$ — $263^{\circ}$ . When boiled with hydrobromic acid, it is reconverted into bromomethyltaurine or with hydriodic acid into iodomethyltaurine. J. J. S.

[3'-Chloro-4'-methylamino-4-hydroxydiphenylamine.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 172079).—*p*-Aminophenol and 2-chloromethylaniline are oxidised with sodium dichromate in acid solution, when the indophenol,  $NHMe\cdot C_6H_3Cl\cdot N:C_6H_4:O$ , thus produced, separates rapidly and partly in a crystalline condition. This colouring matter dissolves in alcohol to an intense blue solution; when treated with warm sodium sulphide in alkaline solution it is reduced, yielding 3'-chloro-4'-methylamino-4-hydroxydiphenylamine,

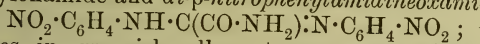


a base which melts at  $105^{\circ}$  and yields a hydrochloride crystallising in greyish-white needles. 3'-Chloro-4'-methylamino-4-ethoxydiphenylamine,  $NHMe\cdot C_6H_3Cl\cdot NH\cdot C_6H_4\cdot OEt$ , melts at  $115^{\circ}$ . Further action of sodium sulphide on these bases at higher temperatures leads to the production of blue sulphur colouring matters. G. T. M.

Transformations of Hydrocyanocarbodiphenylimide. GUSTAV SCHULTZ, GEORG ROHDE, and GUSTAV HERZOG (*J. pr. Chem.*, 1906, [ii], 74, 74—91).—When dissolved in concentrated sulphuric acid, hydrocyanocarbodiphenylimide gradually forms an orange-yellow solution and is regained almost quantitatively on dilution. If the solution in concentrated sulphuric acid is heated on the water-bath, the hydrocyano-compound is partially hydrolysed, yielding phenyloxamide and diphenylamidineoxamide. If the heating is prolonged, the hydrocyanocarbodiphenylimide is hydrolysed to aniline, oxalic acid, and ammonia, the aniline being partially sulphonated; only traces of isatin  $\alpha$ -anilide are formed.

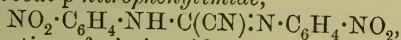
Diphenylamidineoxamide,  $NHPh\cdot C(NPh)\cdot CO\cdot NH_2$ , crystallises in large, glistening, yellow leaflets, melts at  $155^{\circ}$ , and, when heated above its melting point, resolidifies, forming yellow leaflets melting and decomposing at about  $302^{\circ}$ ; the solution in dilute sulphuric acid deposits phenyloxamide slowly at the ordinary temperature, but quickly if heated; when heated with aqueous sodium hydroxide, the amidine-oxamide is hydrolysed, forming aniline, oxalic acid, and ammonia. On treatment with aqueous sodium nitrite in cold concentrated sulphuric acid solution, diphenylamidineoxamide yields phenyloxamide and *p*-nitrophenyloxamide,  $NO_2\cdot C_6H_4\cdot NH\cdot C_2O_2\cdot NH_2$ , which is formed also by the action of aqueous ammonia on ethyl *p*-nitrophenyloxamate. It crystallises from pyridine in slender, yellowish-grey needles, melts and decomposes at  $308$ — $310^{\circ}$ , is stable towards acids, and is hydrolysed by aqueous alkali hydroxides, forming *p*-nitroaniline, oxalic acid, and

ammonia. *Ethyl p-nitrophenyloxamate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , is prepared together with a *product* (*di-p-nitro-oxanilide*?) melting above  $360^\circ$ , by heating a molecular mixture of *p*-nitroaniline and ethyl oxalate in a reflux apparatus; it crystallises in almost colourless, voluminous, long needles, melts at  $171^\circ$ , and is hydrolysed by aqueous sodium hydroxide, forming *p*-nitroaniline, oxalic acid, and ethyl alcohol. The action of nitrogen trioxide or of nitric acid on diphenylamidinoxamide in concentrated sulphuric acid solution leads to the formation of *p*-nitrophenyloxamide and *di-p-nitrophenylamidinoxamide*,

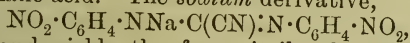


this crystallises in greenish-yellow, transparent prisms, melts and decomposes at  $245^\circ$ , is readily soluble in pyridine, when boiled with glacial acetic acid in a reflux apparatus yields *p*-nitrophenyloxamide, and is hydrolysed by aqueous sodium hydroxide, forming *p*-nitroaniline, oxalic acid, and ammonia.

*Hydrocyanocarbodi-p-nitrophenylimide*,



prepared by the action of nitric acid on hydrocyanocarbodiphenylimide in cooled concentrated sulphuric acid solution, is obtained in two modifications, of which the labile crystallises from dilute solutions in transparent, greenish-yellow, rhombic leaflets or plates, and when heated at  $110^\circ$  changes into the stable form; this is formed on rapid separation from a concentrated solution and crystallises in matted, thin, yellow needles. Both modifications melt and decompose at  $217^\circ$ , and yield *p*-nitrophenyloxamide and *p*-nitroaniline when heated with concentrated sulphuric acid at  $120$ — $140^\circ$ ; hydrolysis by means of boiling dilute sulphuric acid leads to the formation of *p*-nitroaniline, ammonia, and oxalic acid. The *sodium* derivative,



is intensely red and yields the free nitrile when treated with dilute sulphuric acid or persistently washed with water. When heated with aqueous sodium hydroxide, hydrocyanocarbodi-*p*-nitrophenylimide yields small quantities of ammonia and *p*-nitroaniline together with a mixture of two substances, one of which was identified as di-*p*-nitrophenylcarbamide.

When heated with dilute sulphuric acid, hydrocyanocarbodiphenylimide yields aniline and oxanilonitrile (cyanoformanilide), which melts and decomposes at  $128^\circ$  ( $120^\circ$ : Dieckmann and Kaemmerer, Abstr., 1905, i, 874) and is hydrolysed by hot concentrated sulphuric acid, forming phenyloxamide.

The action of sodium nitrite on hydrocyanocarbodiphenylimide in glacial acetic acid solution leads to the formation of *nitrosocyanocarbodiphenylimide*,  $\text{NO} \cdot \text{NPh} \cdot \text{C}(\text{CN}) : \text{NPh}$ , which separates in stout, yellow crystals, melts and decomposes at  $117$ — $118^\circ$ , and gives the reactions of hydrocyanocarbodiphenylimide, into which it decomposes on recrystallisation.

G. Y.

**Additive Products of Derivatives of Trinitrobenzene with Certain Aromatic Nitrogen Compounds.** RICCARDO CIUSA and C. AGOSTINELLI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 238—242).—The phenylhydrazones of acetone, propaldehyde, and camphor, and

probably those of all aliphatic aldehydes and ketones, readily yield crystalline picrates, the formation of which may be used for characterising small quantities of aldehydes and ketones of the aliphatic series.

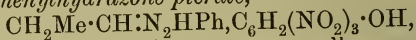
Picryl chloride reacts with propaldehydephenylhydrazone, and probably with the phenylhydrazones of all aliphatic aldehydes and ketones, yielding *s*-picrylphenylhydrazine,  $R\cdot CH:N\cdot N\cdot HPh + H_2O + C_6H_2Cl(NO_2)_3 = R\cdot CHO + HCl + C_6H_2(NO_2)_3\cdot NH\cdot N\cdot HPh$ . With benzalazine, piperonalazine, benzylideneaniline, and cinnamylideneaniline, a similar reaction takes place, whilst with aldazines the corresponding trinitrophenylhydrazones are obtained according to the equation  $CHR:N\cdot N:CHR + H_2O + C_6H_2Cl(NO_2)_3 = HCl + R\cdot CHO + C_6H_2(NO_2)_3\cdot NH\cdot N:CHR$ .

With Schiff's bases, picryl chloride reacts giving the corresponding picrylanilines:  $CHR:NPh + H_2O + C_6H_2Cl(NO_2)_3 = HCl + R\cdot CHO + C_6H_2(NO_2)_3\cdot NHPh$ .

*Acetone phenylhydrazone picrate*,  $CMe_2\cdot N_2HPh, C_6H_2(NO_2)_3\cdot OH$ , crystallises from benzene in unstable, yellow needles melting at  $81-82^\circ$ .

*Camphor phenylhydrazone picrate*,  $C_{10}H_{16}\cdot N_2HPh, C_6H_2(NO_2)_3\cdot OH$ , crystallises in golden-yellow needles melting at  $137^\circ$  to a black liquid.

*Propaldehydephenylhydrazone picrate*,

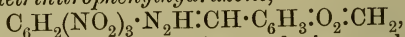


crystallises from alcohol in minute, canary-yellow needles melting at  $156-157^\circ$ .

The interaction of molecular proportions of propaldehydephenylhydrazone and picryl chloride in alcoholic solution yields trinitrohydrazobenzene, which melts at  $186-187^\circ$  ( $183-185^\circ$ : Fischer, *Annalen*, 1889, 252, 2); on boiling with 90 per cent. acetic acid the latter is converted into an isomeric compound, which crystallises in golden-yellow scales melting at  $186^\circ$ , and probably has the structure  $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_3$ .

Picryl chloride and benzalazine yield benzaldehydetrinitrophenylhydrazone, which melts at  $273-274^\circ$ ; Purgotti (Abstr., 1895, i, 27) gave the melting point  $248^\circ$ , and Curtius (Abstr., 1895, i, 30)  $267^\circ$ .

*Piperonaldehydetrinitrophenylhydrazone*,



prepared by the interaction of piperonalazine and picryl chloride, separates from acetic acid in dark red crystals melting at  $169^\circ$ .

The action of picryl chloride on cinnamylideneaniline yields cinnamaldehyde and picrylaniline.

T. H. P.

**Hydrazine Derivatives of the Diaminodiphenylmethane Series.** HERMANN FINGER [with M. BAUMANN] (*J. pr. Chem.*, 1906, [ii], 74, 155-156).—The hydrazine derivatives of *pp'*-diaminodiphenylmethane and diaminoditolylmethane may be prepared by way of the diazosulphonates or the diazonium chlorides.

The potassium diazosulphonate,  $C_{13}H_{10}O_6N_4S_2K_2$ , obtained from *pp'*-diaminodiphenylmethane, separates in slender, yellow needles, and when reduced with zinc dust and boiling acetic acid, yields *pp'*-dihydrazinodiphenylmethane; this forms a white precipitate, crystallises from alcohol, and melts at  $139-140^\circ$ . The hydrochloride,  $C_{13}H_{16}N_4\cdot 2HCl$ ,



forms greyish-white leaflets; the *dinitroso*-derivative is slightly yellow and melts at  $88^{\circ}$ ; the *disemicarbazide* crystallises in silvery leaflets and melts at  $250^{\circ}$ ; the *condensation* product with acetone,  $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{CMe}_2)_2$ , melts at  $90-91^{\circ}$ , and when reduced with zinc chloride forms a *di-indylmethane*,  $\text{CH}_2(\text{C}_6\text{H}_3<\text{CH}>\text{NH})\text{CMe}_2$ , melting at  $170-175^{\circ}$ .

*pp'*-Dihydrazinodiphenylmethane hydrochloride condenses with ethyl acetoacetate, forming a *product* which at  $150^{\circ}$  is converted into the corresponding *pyrazolone* melting at  $210^{\circ}$ . G. Y.

**Preparation of *s*-Secondary Hydrazines from Antipyrines.** LUDWIG KNORR (*Ber.*, 1906, 39, 3265—3267).—*s*-Phenylmethylhydrazine, formed in 85 per cent. yield from antipyrine and alcoholic potash at  $130^{\circ}$ , boils at  $200-201^{\circ}$  under 331 mm. and at  $230^{\circ}$  at the ordinary pressure; the *oxalate*,  $\text{C}_7\text{H}_{10}\text{N}_2\cdot\text{C}_2\text{H}_2\text{O}_4$ , forms slender needles and melts and decomposes at  $155-156^{\circ}$ .

*s*-Phenylethylhydrazine, obtained from 1-phenyl-3-methyl-2-ethylpyrazolone in a similar manner, boils at  $237-240^{\circ}$  under 750 mm. pressure, and forms an *oxalate* which melts and decomposes at  $167-168^{\circ}$ .

1:2:3-Trimethylpyrazolone boils at  $306-309^{\circ}$  under 751 mm. pressure, forms a *platinichloride* which decomposes at  $197-198^{\circ}$ , and a *picrate* which melts and decomposes at  $211-212^{\circ}$ . Alcoholic potash at  $190^{\circ}$  converts the base into *s*-dimethylhydrazine, which boils at  $80-81^{\circ}$  under 753 mm. pressure (compare this vol., i, 817). C. S.

**Crystallographic Constants of 4-Chloropyrazole.** CARLO MARIA VIOLA (*Zeit. Kryst. Min.*, 1906, 42, 384—385).—Determinations are given for this substance, obtained by G. Mazzara and A. Borgo by the action of sulphuryl chloride on pyrazole. L. J. S.

**Preparation of 4:6-Dioxy-2-thiopyrimidine and its 5-Alkyl Substituents.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 171292).—4:6-Dioxy-2-thiopyrimidine,  $\text{CS}<\text{NH}\cdot\text{CO}>\text{CH}_2$ , was prepared by heating 4:6-di-imino-2-thiopyrimidine,  $\text{CS}<\text{NH}\cdot\text{C}(\text{NH})>\text{CH}_2$ , with 30 per cent. sulphuric acid.

4:6-Dioxy-2-thio-5-diethylpyrimidine,  $\text{CS}<\text{NH}\cdot\text{CO}>\text{C}_2\text{H}_5$ , was obtained in a similar manner from 4:6-diamino-2-thio-5:5-diethylpyrimidine (compare *Abstr.*, 1905, i, 671). G. T. M.

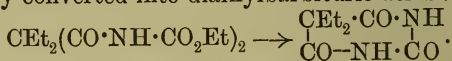
**Preparation of Barbituric Acid and its 5-Alkyl Derivatives.** CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 171294).—Ethyl malonamate and urethane were condensed by heating on the water-bath with alcoholic sodium ethoxide, and the resulting barbituric acid precipitated from the acidified solution. The corre-

sponding *C*-alkyl derivatives were similarly prepared from the mono- and di-alkylmalonamates. G. T. M.

**Preparation of 5:5-Dialkylbarbituric Acid.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 170907).—The 5:5-dialkylbarbituric acids are obtained from the corresponding thio-derivatives by heating these with solutions of the salts of the heavy metals.

Diethylthiobarbituric acid, when boiled for twenty-four to forty-eight hours with solutions of lead acetate or copper chloride, yielded a precipitate of the metallic sulphide, and the diethylbarbituric acid was then isolated on concentrating the filtered solution. G. T. M.

**Preparation of 5:5-Dialkylbarbituric Acids.** WILHELM TRAUBE (D.R.-P. 171992).—The diurethane derivatives of the dialkylmalonic acids are produced by heating the dialkylmalonyl chlorides with urethanes:  $\text{CEt}_2(\text{COCl})_2 + 2\text{NH}_2\cdot\text{CO}_2\text{Et} = \text{CEt}_2(\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2 + 2\text{HCl}$ . These products, when heated at temperatures varying from 80° to 150° with metallic alkyloxides, either alone or in alcoholic solution, are readily converted into dialkylbarbituric acids:



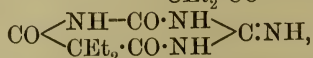
For example, 30 parts of diethylmalonylurethane, when heated with 7 to 20 parts of dry sodium ethoxide for one or two hours at 80–100° and then at 150°, and subsequently treated with dilute acid, yield diethylbarbituric acid melting at 191°. G. T. M.

**Preparation of 5:5-Dialkylbarbituric Acids.** WILHELM TRAUBE (D.R.-P. 172885, 172886. Compare this vol., i, 538, and preceding abstracts).—Instead of heating the dialkylmalonyldiurethanes with metallic alkyloxides, the conversion of these substances into 5:5-dialkylbarbituric acids may be readily effected by heating with alcoholic or aqueous alkali hydroxides or with concentrated or fuming sulphuric acid. This transformation may likewise be carried out by the agency of aqueous or alcoholic ammonia or organic bases.

Diethylmalonyldiurethane mixed with ordinary concentrated sulphuric acid is added to fuming sulphuric acid and heated at 100° for some time. On pouring the solution into ice-cold water, 5:5-diethylbarbituric acid separates as an oil which rapidly solidifies. This acid is also formed when the diurethane is boiled with alcoholic potash, soda, ammonia, or any organic base such as guanidine, pyridine, or an alkylamine. G. T. M.

**Preparation of Guanyldiethylbarbituric Acid.** CHEMISCHE FABRIK VON HEYDEN AKTIEN-GESELLSCHAFT (D.R.-P. 171147).—

*Guanyldiethylbarbituric acid*,  $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \text{CEt}_2 \text{---} \text{CO} \end{array} \text{N}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$  or

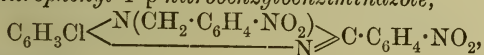


is prepared by heating together ethyl diethylmalonate and dicyanodiamidine hydrochloride in alcoholic sodium ethoxide and slightly acidifying the solution; when crystallised from hot, dilute hydrochloric acid, it separates in well-defined prisms. Prolonged boiling with

mineral acids hydrolyses the guanyl derivatives to diethylbarbituric acid. The condensation may also be effected by means of sodamide or metallic sodium. G. T. M.

**Benziminazoles and their Resolution.** OTTO FISCHER and FRITZ LIMMER (*J. pr. Chem.*, 1906, [ii], 74, 57—73. Compare Fischer and Hess, *Abstr.*, 1904, i, 195; Fischer, this vol., i, 539).—*p*-Chlorodibenzylidene-*o*-phenylenediamine,  $C_6H_5Cl(N:CHPh)_2$ , formed from *p*-chloro-*o*-phenylenediamine and benzaldehyde at 150—170°, crystallises in colourless, nodular aggregates, melts at about 168°, and on prolonged heating above its melting point yields 6-chloro-2-phenyl-1-benzylbenziminazole,  $C_6H_5Cl \langle \underset{N}{\overset{N(CH_2Ph)}{}} \rangle CPh$ , which crystallises from alcohol in white needles and volatilises at about 225°. The hydrochloride forms slender, white needles; the *platinichloride* crystallises in short, yellow needles; the *nitrate* crystallises in long, colourless prisms.

*p*-Chlorodi-*p*-nitrobenzylidene-*o*-phenylenediamine, prepared from *p*-chloro-*o*-phenylenediamine and *p*-nitrobenzaldehyde, crystallises in red leaflets, melts at about 150°, and gradually becomes yellow, forming 6-chloro-2-*p*-nitrophenyl-1-*p*-nitrobenzylbenziminazole,



which melts at 235°.

The product obtained on shaking *p*-chloro-*o*-phenylenediamine with ethyl acetoacetate in alcoholic solution crystallises in long, white needles, melts at 140°, forms a *nitrobenzylidene* derivative crystallising in reddish-yellow needles and melting at 210°, and on prolonged heating above its melting point is converted into ethyl acetate and 6-chloro-2-methylbenziminazole,  $C_6H_5Cl \langle \underset{N}{\overset{NH}{}} \rangle CMe$ , which melts at 203°.

*p*-Chlorodiphenylquinoxaline,  $C_{20}H_{13}N_2Cl$ , prepared by heating a molecular mixture of *p*-chloro-*o*-phenylenediamine and benzil at 100°, crystallises in colourless, refracting leaflets, melts at 130°, and gives a red coloration with concentrated sulphuric acid.

*p*-Chloro-*o*-phenylenethiocarbamide,  $C_6H_5Cl \langle \underset{NH}{\overset{NH}{}} \rangle CS$ , prepared by boiling *p*-chloro-*o*-phenylenediamine with a concentrated aqueous solution of ammonium thiocyanate and a small quantity of hydrochloric acid and heating the product at 130—150°, crystallises in colourless needles, melts above 270°, is almost insoluble in water, but dissolves readily in alcohol, and has a bitter taste.

*p*-Chloro-*o*-phenylenecarbamide,  $C_6H_5Cl \langle \underset{NH}{\overset{NH}{}} \rangle CO$ , obtained by heating *p*-chloro-*o*-phenylenediamine with phosgene in toluene solution, crystallises in small, white needles, melts above 270°, and has a bitter taste.

*p*-Chloronitrodiacetyl-*o*-phenylenediamine,  $C_{10}H_{10}O_4N_3Cl$ , is prepared by adding *p*-chlorodiacyl-*o*-phenylenediamine, which melts at 208° (201°: Ullmann and Mauthner, *Abstr.*, 1904, i, 192) to red, fuming nitric acid; it crystallises in stellate aggregates of needles, softens at



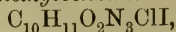
about 240°, melts and decomposes at 245°, has weak basic and acid properties, and gives a deep red coloration with concentrated alkali hydroxides.

*p*-Chlorodibenzoyl-*o*-phenylenediamine,  $C_{20}H_{15}O_2N_2Cl$ , formed by fusing the *o*-diamine with benzoic anhydride, crystallises in soft, silky needles, melts at 230°, and is insoluble in dilute acids or alkali hydroxides. *p*-Chloronitrodibenzoyl-*o*-phenylenediamine, prepared by the action of fuming nitric acid on the preceding substance, crystallises in nodular aggregates of almost colourless needles, melts at 209—210°, dissolves in concentrated hydrochloric or sulphuric acid, and with concentrated potassium hydroxide gives a red coloration, becoming yellow on exposure to air.

6-Chloronitrobenziminazole,  $NO_2 \cdot C_6H_2Cl \left\langle \begin{smallmatrix} NH \\ N \end{smallmatrix} \right\rangle CH$ , prepared by dissolving 6-chlorobenziminazole (Fischer, Abstr., 1904, i, 349) in red, fuming nitric and concentrated sulphuric acids, crystallises in small, slightly yellow needles, melts at 180—181°, and is readily soluble in cold aqueous alkali hydroxides or ammonia, mineral acids, glacial acetic acid, or hot alcohol. When heated with methyl iodide and methyl alcohol in a sealed tube at 110°, it yields the quaternary iodide,  $NO_2 \cdot C_6H_2Cl \left\langle \begin{smallmatrix} N(MeI) \\ NMe \end{smallmatrix} \right\rangle CH$ , which crystallises in yellow prisms, and the periodide,  $C_9H_9O_2N_3ClI_3$ , which is obtained in blue, glistening prisms, and loses  $I_2$  when boiled with water, or more quickly when treated with sulphur dioxide or aqueous alkali hydroxides. 6-Chloronitro-1:3-dimethylbenziminazolol,  $NO_2 \cdot C_6H_2Cl \left\langle \begin{smallmatrix} NMe \\ NMe \end{smallmatrix} \right\rangle CH \cdot OH$ , prepared by heating the quaternary iodide with an aqueous alkali hydroxide, crystallises from alcohol in yellow leaflets, becomes brown at about 190°, melts and decomposes at about 215°, and is moderately soluble in hot water. *p*-Chloronitrodimethyl-*o*-phenylenediamine,  $C_8H_{10}O_2N_3Cl$ , obtained on boiling the carbinol with alcoholic potassium hydroxide for half an hour, crystallises in red prisms, melts at 220°, forms a yellow ferrichloride and a hydrochloride crystallising in slender, yellow needles, regenerates the benziminazolol when boiled with concentrated formic acid, and yields 6-chloronitro-1:2:3-trimethylbenziminazole when boiled with glacial acetic acid and acetic anhydride.

6-Chloronitro-2-methylbenziminazole,  $NO_2 \cdot C_6H_2Cl \left\langle \begin{smallmatrix} NH \\ N \end{smallmatrix} \right\rangle CMe$ , prepared by heating *p*-chloronitrodiacetyl-*o*-phenylenediamine with concentrated hydrochloric acid on the water-bath, or by nitrating 6-chloro-2-methylbenziminazole, crystallises from dilute alcohol in almost colourless needles, melts at 210°, and is readily soluble in aqueous alkali hydroxides, ammonia, glacial acetic acid, or alcohol. The aurichloride forms large, golden prisms, the platinichloride, long, light-yellow needles, and the picrate, long, yellow prisms melting at 221°.

6-Chloronitro-1:2:3-trimethylbenziminazolium iodide,

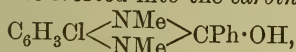


formed together with the brown, crystalline periodide when 6-chloro-

nitro-2-methylbenziminazole is heated with methyl iodide and methyl alcohol at  $110^\circ$  under pressure, crystallises in long, yellow needles and melts at  $263^\circ$ . 6-Chloronitro-1:2:3-trimethylbenziminazolol,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Cl} \langle \text{NMe} \rangle \text{CMe} \cdot \text{OH}$ , prepared by gently heating the quaternary iodide with aqueous potassium hydroxide, crystallises from hot alcohol in glistening, yellow leaflets, becomes brown at about  $190^\circ$ , melts at about  $205^\circ$ , and when boiled with alcoholic potassium hydroxide is hydrolysed, yielding acetic acid and *p*-chloronitrodimethyl-*o*-phenylenediamine.

6-Chloro-2-phenylbenziminazole,  $\text{C}_6\text{H}_3\text{Cl} \langle \text{NH} \rangle \text{CPh}$ , prepared by heating *p*-chlorodibenzoyl-*o*-phenylenediamine with concentrated hydrochloric acid at  $160^\circ$  under pressure, crystallises in glistening, colourless leaflets, melts at  $210^\circ$ , and is readily soluble in alcohol, hot ether, chloroform, or hot aqueous alkali hydroxides.

The quaternary iodide,  $\text{C}_6\text{H}_3\text{Cl} \langle \text{N(MeI)} \rangle \text{CPh}$ , forms glistening leaflets, melts at  $263^\circ$ , and when boiled with aqueous or alcoholic potassium hydroxide is converted into the *carbinol*,



which crystallises from dilute alcohol in colourless, quadratic prisms, melts at  $140^\circ$ , and is only slightly hydrolysed by boiling alcoholic potassium hydroxide.

6-Chloronitro-2-phenylbenziminazole,  $\text{C}_{13}\text{H}_8\text{O}_2\text{N}_3\text{Cl}$ , prepared from *p*-chloronitrodibenzoyl-*o*-phenyldiamine or by nitration of 6-chloro-2-phenylbenziminazole, crystallises in yellow needles, melts at  $255^\circ$ , and is readily soluble in hot alcohol, glacial acetic acid, or aqueous alkali hydroxides or ammonia. 6-Chloro-2-phenyl-1:3-dimethylbenziminazolium iodide crystallises in colourless needles and melts at  $265\text{--}266^\circ$ . The *carbinol*,  $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_3\text{Cl}$ , crystallises in glistening, golden leaflets, melts at  $188^\circ$ , and on prolonged boiling with alcoholic potassium hydroxide yields benzoic acid and *p*-chloronitrodimethyl-*o*-phenylenediamine.

Huebner's nitrophenylbenziminazole (Abstr., 1881, 1131) is 6-nitro-2-phenylbenziminazole,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \langle \text{NH} \rangle \text{CPh}$ , as on methylation it yields a quaternary iodide,  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_3\text{I}$ , which crystallises in stellate groups of needles, melts at  $249^\circ$ , and when boiled with alcoholic potassium hydroxide is converted into 6-nitro-2-phenyl-1:3-dimethylbenziminazolol,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \langle \text{NMe} \rangle \text{CPh} \cdot \text{OH}$ ; this crystallises in golden leaflets, melts at  $192^\circ$ , and on hydrolysis yields benzoic acid and *m*-nitrodimethyl-*o*-phenylenediamine.

2-*o*-Nitrophenyl-1:3-dimethylbenziminazolium iodide,  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_3\text{I}$ , prepared from 2-*o*-nitrophenylbenziminazole, crystallising in colourless prisms (brown leaflets: Walther and Pulawski, Abstr., 1899, i, 639), crystallises in red, dichroic octahedra, forms a yellow powder when pulverised, melts above  $280^\circ$ , and when warmed with aqueous potassium hydroxide forms the *carbinol*. This crystallises in large,

orange prisms, melts at  $210^{\circ}$ , and yields only traces of *s*-dimethyl-*o*-phenylenediamine on prolonged boiling with alcoholic potassium hydroxide.

*2-m-Nitrophenyl-1:3-dimethylbenziminazolium iodide* crystallises in flat, yellow needles and melts at high temperatures. *2-m-Nitrophenyl-1:3-dimethylbenziminazolol*,  $C_{15}H_{15}O_3N_3$ , crystallises in yellow needles, melts at  $167^{\circ}$ , and is hydrolysed to only a slight extent when boiled with alcoholic potassium hydroxide for several hours.

*2-p-Nitrophenylbenziminazole* melts at  $210^{\circ}$  (compare Walther and Pulawski, *loc. cit.*); the quaternary iodide formed by heating with methyl iodide crystallises in long, yellow needles, melts above  $270^{\circ}$ , and when treated with an alkali hydroxide yields *2-p-nitrophenyl-1:3-dimethylbenziminazolol*, which crystallises in yellow prisms and melts at  $140^{\circ}$ .

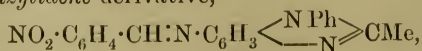
The yellow quaternary iodides described above form colourless aqueous solutions. G. Y.

**Some Benziminazoles from 4:2-Nitroaminodiphenylamine.** REINHOLD VON WALTHER and ALEX. KESSLER (*J. pr. Chem.*, 1906, [ii], 74, 188—206, 241—248. Compare Abstr., 1904, i, 348).—The *hydrochloride* of 5-nitro-1-phenyl-2-methylbenziminazole crystallises in glistening leaflets and melts at  $228^{\circ}$ ; the *picrate*,

$C_{14}H_{11}O_2N_3 \cdot C_6H_3O_7N_3$ , forms yellow needles and does not melt at  $270^{\circ}$ ; the *methiodide*,  $NO_2 \cdot C_6H_3 \left\langle \begin{smallmatrix} NPh \\ N(MeI) \end{smallmatrix} \right\rangle CMe$ , crystallises in yellow prisms and commences to decompose at  $270^{\circ}$ . *5-Nitro-1-phenyl-2:3-dimethylbenziminazolol*,  $NO_2 \cdot C_6H_3 \left\langle \begin{smallmatrix} NPh \\ NMe \end{smallmatrix} \right\rangle CMe \cdot OH$ , prepared by heating the methiodide with aqueous sodium hydroxide, crystallises from benzene in yellow needles, melts at  $206^{\circ}$ , and is not hydrolysed by boiling alcoholic potassium hydroxide.

*5-Amino-1-phenyl-2-methylbenziminazole*,  $NH_2 \cdot C_6H_3 \left\langle \begin{smallmatrix} NPh \\ N \end{smallmatrix} \right\rangle CMe$ , prepared by reduction of the 5-nitro-compound by means of alcoholic ammonium sulphide at  $120^{\circ}$  under pressure, crystallises from a mixture of ethyl acetate and light petroleum in yellowish-brown needles, melts at  $145$ — $147^{\circ}$ , and is a strong base dissolving readily in dilute acids. The *picrate*,  $C_{14}H_{13}N_3 \cdot C_6H_3O_7N_3$ , melts at  $195^{\circ}$ ; the *platinichloride*,  $NHAc \cdot C_7N_2H_3PhMe$ , crystallises in white needles and melts at  $229$ — $230^{\circ}$ . The *benzeneazo-derivative*,  $NPh:N \cdot NH \cdot C_7N_2H_3PhMe$ , formed by adding a freshly-prepared solution of diazobenzene chloride and sodium acetate to the amine in cooled hydrochloric acid solution, crystallises in yellowish-red needles, melts at  $184$ — $185^{\circ}$ , is insoluble in aqueous sodium hydroxide, evolves nitrogen when heated with hydrochloric acid, and decomposes on prolonged heating with alcohol.

The *p-nitrobenzylidene derivative*,

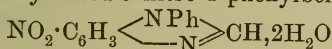




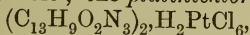
formed by boiling the amine with *p*-nitrobenzaldehyde in alcoholic solution in a reflux apparatus, crystallises in yellow needles and melts at 240°. The *o*-nitrobenzylidene derivative,  $C_{21}H_{16}O_2N_4$ , crystallises from alcohol in green needles and melts at 153—155°.

When heated with resorcinol at 175°, 5-amino-1-phenyl-2-methylbenziminazole forms an *additive* compound,  $C_{14}H_{13}N_3 \cdot C_6H_4(OH)_2$ , which crystallises from dilute alcohol in silver-grey needles and melts at 197°. The *thiocarbamide*,  $CS(NH \cdot C_7N_2H_3PhMe)_2$ , prepared by heating the amine with carbon disulphide and a small quantity of flowers of sulphur in alcoholic solution in a sealed tube at 100°, crystallises from dilute alcohol in white needles, sinters at 130°, and melts and decomposes at 141°. 5-Phenylcarbamido-1-phenyl-2-methylbenziminazole,  $NHPh \cdot CO \cdot NH \cdot C_7N_2H_3PhMe$ , formed by the action of phenylcarbimide on the amine in ethereal solution, crystallises from alcohol and melts and decomposes at 140—143°.

4-Nitro-2-formylaminodiphenylamine,  $CHO \cdot NH \cdot C_6H_3(NO_2) \cdot NHPh$ , prepared by the action of anhydrous formic acid on 4-nitro-2-aminodiphenylamine at the ordinary temperature, crystallises from alcohol in golden needles, melts at 182°, and gives a characteristic deep violet coloration with concentrated sulphuric acid. When heated with 40 per cent. sulphuric acid on the water-bath, 4-nitro-2-formylaminodiphenylamine yields hydrated 5-nitro-1-phenylbenziminazole,

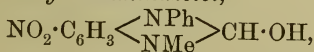


(compare Reissert and Goll, *Abstr.*, 1905, i, 247), which crystallises in colourless needles and melts at 134°; the anhydrous benziminazole obtained by heating the hydrated substance on the water-bath, or recrystallising it from alcohol, or by heating 4-nitro-2-aminodiphenylamine with an excess of ethyl-*o*-formate in a reflux apparatus on the water-bath, or by heating 4-nitro-2-formylaminodiphenylamine with hydrochloric acid, crystallises in colourless needles and melts at 156°. The *nitrate*,  $C_{13}H_9O_2N_3 \cdot HNO_3$ , crystallises in white needles, melts at 205°, and is sparingly soluble; the *platinichloride*,

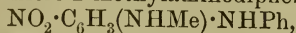


forms yellow needles; the *methiodide*,  $NO_2 \cdot C_6H_3 \begin{array}{c} \text{NPh} \\ \diagup \quad \diagdown \\ \text{---} \text{N}(\text{MeI}) \end{array} \text{CH}$ , crystallises in stout, yellow needles and commences to melt and decompose at 245°.

5-Nitro-1-phenyl-3-methylbenziminazolol,



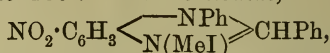
obtained by treating the methiodide with sodium hydroxide in cooled aqueous solution, crystallises in yellow needles and melts at 200°. When heated with alcoholic potassium hydroxide, the methiodide is hydrolysed, forming 4-nitro-2-methylaminodiphenylamine,



which crystallises from alcohol, is yellow, and melts at 155—156°. It is converted by boiling with acetic anhydride in glacial acetic solution into 5-nitro-1-phenyl-2 : 3-dimethylbenziminazolol, melting at 206°.

When heated with concentrated hydrochloric acid at 150°, 4-nitro-2-benzoylaminodiphenylamine, prepared by boiling 4-nitro-2-aminodi-

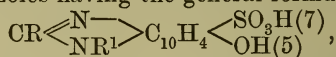
phenylamine with benzoic anhydride in alcoholic solution (compare Muttelet, Abstr., 1898, i, 412), is converted into the insoluble *hydrochloride* of 5-nitro-1 : 2-diphenylbenziminazole,  $C_{19}H_{13}O_2N_2 \cdot HCl$ , which crystallises in silvery needles melting at  $236^\circ$ ; the base melting at  $181$ — $182^\circ$  is formed when 4-nitro-2-benzoylamino-diphenylamine is heated with dilute sulphuric acid at  $100^\circ$  and treated with concentrated sulphuric acid, or when 4-nitro-2-aminodiphenylamine is heated with benzoic anhydride at  $180^\circ$ . The *methiodide*,



crystallises from methyl alcohol in yellow needles, commences to melt and decompose at  $260^\circ$ , and when treated with potassium hydroxide in hot methyl-alcoholic solution yields the yellow carbinol (?) melting at  $190^\circ$ , and, on further heating, 4-nitro-2-aminodiphenylamine.

5-Amino-1 : 2-diphenylbenziminazole, prepared by reduction of the 5-nitro-base with zinc dust and alcoholic hydrogen chloride, forms an *acetyl* derivative,  $NHAc \cdot C_6H_3 \begin{array}{c} \text{NPh} \\ \text{N} \end{array} CPh$ , which crystallises in glistening needles and melts at  $254^\circ$ . G. Y.

[Hydroxynaphthiminazoles and their Azo-derivatives.] FARENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 172319).—The hydroxynaphthiminazoles having the general formula



where R and  $R^1$  are either hydrogen atoms or aliphatic or aromatic groups, are produced by the action of aldehydes or mixtures in molecular proportion of aldehydes and ketones, or of acid anhydrides or chlorides, on 5-hydroxy-1 : 2-naphthylenediamine-7-sulphonic acid. When acid anhydrides or chlorides are employed, the acyl derivative first obtained is heated with acids, when the iminazole ring is formed.

$\mu$ -Methyl-1 : 2-naphthiminazole-5-hydroxy-7-sulphonic acid is prepared by treating a neutral solution of 5-hydroxy-1 : 2-naphthylenediamine-7-sulphonic acid with acetic anhydride. When the solution no longer gives a coloration with sodium nitrite, it is heated to boiling and finally cooled, when the new compound crystallises out. By replacing acetic anhydride by benzoyl or *p*-nitrobenzoyl chloride in the foregoing condensation, 5-hydroxy- $\mu$ -phenyl-1 : 2-naphthiminazole-7-sulphonic acid and the corresponding *p*-nitrophenyl derivative are produced.

Phthalic anhydride may likewise be employed when  $\mu$ -carboxyphenyl-1 : 2-naphthiminazole-5-hydroxy-7-sulphonic acid is formed.

G. T. M.

**Molecular Weight of Indigotin.** ERNST BECKMANN and WERNER GABEL (*Ber.*, 1906, 39, 2611—2618).—The authors have extended the experiments of Vaubel (Abstr., 1901, i, 714; 1902, i, 542) on the molecular weight of indigotin. Whilst Vaubel found, by the cryoscopic method with phenol and *p*-toluidine respectively, a molecular weight for indigotin corresponding with twice the value demanded by the Baeyer formula, the ebullioscopic determinations now quoted by the authors gave values corresponding with the single formula. The solvents used were quinoline, aniline, phenol, and *p*-toluidine.

The molecular rises of the boiling point of phenol and *p*-toluidine respectively were redetermined and found to be  $34\cdot40^\circ$  and  $41\cdot40^\circ$ .

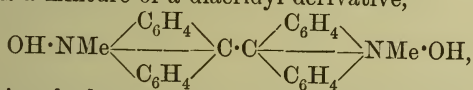
Cryoscopic measurements with aniline and with phenol gave values corresponding with the single formula. Whilst the authors' results with phenol are at variance with Vaubel's, the results with *p*-toluidine agree.

A. McK.

**Molecular Weight of Indigotin.** HERMANN WICHELHAUS (*Ber.*, 1906, 39, 3298. Compare Beckmann and Gabel, preceding abstract).—The author draws attention to his determination of the molecular weight of  $\alpha$ -naphthaleneindigo (*Abstr.*, 1894, i, 42).

G. Y.

**Reduction of Cyclic Amine-ones. I. Preparation of Acridine from Acridone.** HERMAN DECKER and GEORGES DUNANT (*Ber.*, 1906, 39, 2720—2722).—When reduced with zinc and acetic acid, 10-methylacridone yields a mixture of a diacridyl derivative,



methylacridonium hydroxide, and methyl dihydroacridine. The last is readily oxidised by 2 per cent. nitric acid to a methylacridonium nitrate.

As the acridonium salts are readily converted into acridine and methyl esters, these processes afford a convenient method for transforming acridone into acridine.

J. J. S.

**Action of Imino-ethers on Amino-esters.** HERMANN FINGER and L. SCHUPP (*J. pr. Chem.*, 1906, [ii], 74, 154).—4-Keto-2-phenyl-1:4-dihydroquinazoline, melting at  $241^\circ$ , is formed when a molecular mixture of benziminoethyl ether and methyl anthranilate is heated.

Imino-ethers condense in the same manner with  $\alpha$ - and  $\beta$ -amino-esters of the fatty series.

G. Y.

**Diacridines.** CARLO BAEZNER [in part with J. GUEORGUEFF and AUGUST GARDIOL] (*Ber.*, 1906, 39, 2650—2653. Compare this vol., i, 699, 887).—In the preparation of hydroxynaphthacridines by the reduction of *o*-nitrobenzyl chlorides with stannous chloride in the presence of dihydroxynaphthalenes, substances were obtained as by-products which were insoluble in alkali. These products became the main products of the action when the nitro-compound was used in the proportion of 2 mols. to 1 mol. of naphthol.

3':3"-Diamino-2:7-naphthalenediacridine,  $\text{C}_{24}\text{H}_{16}\text{N}_4$ , is obtained from *o-p*-dinitrobenzyl chloride and 2:7-dihydroxynaphthalene, whilst 3'-amino-7-hydroxy-1:2-phenonaphthacridine is also obtained. The former separates from nitrobenzene in yellowish-red needles and decomposes at  $360^\circ$ . Its salts with mineral acids are highly coloured. Its diacetyl derivative separates from nitrobenzene in yellow needles and melts at  $240$ — $245^\circ$ .

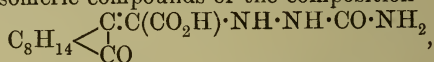
3':3"-Diamino-2:3-naphthalenediacridine,  $\text{C}_{24}\text{H}_{16}\text{O}_4$ , obtained from *o-p*-dinitrobenzyl chloride and 2:3-dihydroxynaphthalene, separates from xylene in greyish-yellow needles. Its solution in concentrated sulphuric acid is yellow and exhibits bluish-green fluorescence. Its



*hydrochloride* separates from dilute hydrochloric acid in violet-red crystals.

The reduction of *o*-nitrobenzyl chloride in presence of 2:7-dihydroxynaphthalene yielded, in addition to 7-hydroxy-1:2-phenonaphthacridine, a product insoluble in alkali but partly soluble in xylene. From the xylene solution a compound  $C_{24}H_{18}ON_2$  was isolated; it melted at 123—125°. A. McK.

**Action of Amines on Camphoroxalic Acid.** J. BISHOP TINGLE and CHARLES J. ROBINSON (*Amer. Chem. J.*, 1906, 36, 223—290).—By the action of semicarbazide on camphoroxalic acid, J. B. and A. Tingle (Abstr., 1900, i, 302) obtained a product which seemed to consist of two isomeric compounds of the composition



which melted at 218° and 209—210° respectively. Tingle and Hoffman (Abstr., 1905, i, 800) obtained a similar compound which they termed semicarbazidocamphoformeneaminecarboxylic acid, which on crystallisation from alcohol melted at 200°, but when crystallised from glacial acetic acid melted at 209—210°. These experiments have been repeated and the apparently isomeric substances have been proved to be identical, the differences observed in the melting point being due to differences in the rate of heating. When camphoroxalic acid is heated with semicarbazide at 125° under pressure, hydrazodicarbamide and camphylpyrazolecarboxylic acid are obtained. The same compounds, together with camphyl-3-keto-1:2:4-heptatriazine, are produced when carbamylcamphoformeneaminecarboxylic acid (semicarbazidocamphoformeneaminecarboxylic acid) is heated at its melting point for twenty minutes.

*Camphylpyrazolecarboxylic acid*,  $C_8H_{14} \begin{array}{l} \diagup C \text{---} C \cdot CO_2H \\ \diagdown \begin{array}{l} | \\ C \cdot NH \cdot N \end{array} \end{array}$ , forms stout, colourless, prismatic crystals, melts at 255—258°, and is soluble in alcohol or acetone and slightly so in hot water. On fusion, it is converted into *camphylpyrazole*,  $C_8H_{14} \begin{array}{l} \diagup C \cdot CH \\ \diagdown \begin{array}{l} | \\ C \cdot NH \end{array} \end{array} \gg N$ , which remains unmelted at 288°.

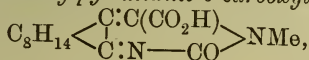
*Camphyl-3-keto-1:2:4-heptatriazine*,  $C_8H_{14} \begin{array}{l} \diagup C \cdot CH \cdot NH \\ \diagdown \begin{array}{l} | \\ C = N \cdot CO \end{array} \end{array} \gg NH$ , crystallises from alcohol in small, yellow prisms, melts at 305—306°, and is sparingly soluble in ether, acetone, benzene, or light petroleum.

Ethyl carbamylcamphoformeneaminecarboxylate (J. B. Tingle and A. Tingle, *loc. cit.*) melts at 191°, but the melting point varies with the rate of heating. If the ester is left in contact with the alcoholic hydrogen chloride solution in which it was produced, it undergoes decomposition with formation of *ethyl camphylpyrazolecarboxylate*, which crystallises from light petroleum in large, hemimorphic, monoclinic prisms and melts at 91—92°; its *hydrochloride* softens at 151° and melts at 156°.

When an alcoholic solution of camphoroxalic acid and carbamide is

heated under pressure at 135°, *formamidylcamphorformeneaminecarboxylic acid*,  $C_8H_{14} \begin{smallmatrix} & C:C(CO_2H) \cdot NH \cdot CO \cdot NH_2 \\ & | \\ & CO \end{smallmatrix}$ , is produced, which melts and decomposes at 192—194° and is readily soluble in alcohol and sparingly so in acetone, ethyl acetate, or chloroform.

Methylcarbamide reacts with camphoroxalic acid with formation of *2-keto-4:5-camphyl-1-methylpyrimidine-6-carboxylic acid*,



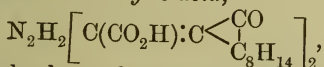
which crystallises in long, pale yellow prisms, melts at 154°, and dissolves readily in ether, acetone, chloroform, or hot alcohol.

By the interaction of *s*-dimethylcarbamide and camphoroxalic acid, a small quantity of a substance melting at 104—105° is obtained, together with a larger amount of *methylcamphorformeneaminecarboxylic acid*,  $C_8H_{14} \begin{smallmatrix} & C:C(CO_2H) \cdot NHMe \\ & | \\ & CO \end{smallmatrix}$ , which crystallises in long, colourless,

prismatic needles, melts at 77—78°, and is very soluble in the usual organic solvents. Attempts were made to obtain condensation products of camphoroxalic acid and *as*-dimethylcarbamide, but without success.

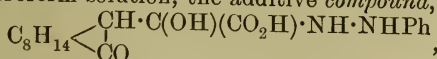
Camphoroxalic acid reacts with a solution of hydrazine in methyl alcohol at the ordinary temperature with formation of hydrazine camphoroxalate, biscamphorformeneaminecarboxylic acid, and camphylpyrazolecarboxylic acid. *Hydrazine camphoroxalate*,  $N_2H_4 \cdot 2C_{12}H_{16}O_4$ , is a pale yellow salt which begins to decompose at 186° and is completely melted at 245°.

*Biscamphorformeneaminecarboxylic acid*,



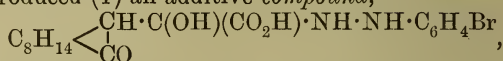
crystallises in long, slender, pale yellow needles with 2 mols. of methyl alcohol, which it loses at 100° and becomes deep yellow; on further heating it begins to decompose at 137°, and is not completely melted at 155°. When the acid is heated at 150—155°, carbon dioxide is evolved and a product is obtained from which the following three substances were isolated. (1) A compound,  $C_{24}H_{30}O_6N_2$ , which crystallises in clusters of pale yellow needles, melts at 222—223° and has acid properties. (2) A compound, isomeric with the preceding substance, which has a dull yellow colour and melts at 232°; solutions of this compound gradually turn red and deposit red crystals which also melt at about 232°. (3) A compound,  $C_{24}H_{30}O_5N_2$ , which crystallises in light yellow prisms and melts at 221°.

When phenylhydrazine (2 mols.) is added to camphoroxalic acid (1 mol.) in chloroform solution, the additive compound,



is produced, which crystallises in slender, yellow needles, melts at 120°, and is very stable. If the compound is fused or boiled with alcohol, it is converted into camphylphenylpyrazolecarboxylic acid (Abstr., 1897, i, 484), which melts at 196° and crystallises with 1 mol. of alcohol.

By the action of *p*-bromophenylhydrazine on camphoroxalic acid, there are produced (1) an additive compound,



which crystallises in slender, yellow needles, melts at  $149^\circ$ , and is very stable, and (2) a compound,  $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}_2\text{Br}$ , which melts at  $172^\circ$ . When either of these substances is fused, *camphyl-p-bromophenylpyrazolecarboxylic acid*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} - \text{C}(\text{CO}_2\text{H}) \\ \parallel \quad \parallel \\ \text{C} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \end{array} \text{N}$ , is produced which

crystallises from benzene in clusters of minute, colourless needles and melts at  $215^\circ$ ; the *ethyl* ester separates from acetone in triclinic crystals, melts at  $149^\circ$ , and, unlike ethyl camphylpyrazolecarboxylate, does not possess basic properties. When this acid is heated at its melting point, carbon dioxide is evolved, and a compound, probably

*camphyl-p-bromophenylpyrazole*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} - \text{CH} \\ \parallel \quad \parallel \\ \text{C} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \end{array} \text{N}$ , is obtained, which is very soluble in the ordinary organic solvents and, on evaporating its solutions, remains as a gummy mass.

On investigating the hydration product of camphoroxalic acid (Abstr., 1898, i, 443), evidence was obtained that the water is not present as water of crystallisation. The hydration product reacts with aniline and with semicarbazide with formation of substances identical with those obtained from the acid itself. With hydroxylamine, the hydration product yields a substance which melts at  $181-182^\circ$ .

A table is given showing the relations between the various derivatives of camphoroxalic acid which have been obtained by the action of amines, and a summary is made of the various facts which support the conclusion that camphoroxalic acid has the keto-enolic structure represented by the formula  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} : \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \\ \parallel \\ \text{CO} \end{array}$ . E. G.

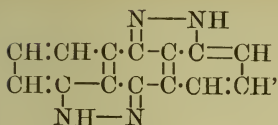
**Preparation of Pyrazoles from Anthraquinone Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 171293).—The

*pyrazole* derivative,  $\begin{array}{c} \text{CH} : \text{CH} \cdot \text{C} \cdot \text{CO} - \text{C}(\text{OH}) : \text{CH} \\ \parallel \quad \parallel \\ \text{CH} : \text{CH} \cdot \text{C} \cdot \text{C} - \text{C} = \text{CH} \\ \parallel \quad \parallel \\ \text{N} - \text{NH} \end{array}$ , is produced by heat-

ing 4-hydrazino-1-hydroxyanthraquinone hydrochloride with aniline and aniline hydrochloride at  $170-180^\circ$ . At first a molecular compound of the substance with aniline is obtained, but the base is removed on washing with solvents. This pyrazole derivative dissolves in concentrated sulphuric acid or aqueous sodium hydroxide to a yellow solution having an intense green fluorescence.

The *monopyrazole* derivative,  $\begin{array}{c} \text{CH} : \text{CH} - \text{C} - \text{C} = \text{CH} \\ \parallel \quad \parallel \quad \parallel \\ \text{CH} : \text{C}(\text{NH} \cdot \text{NH}_2) \cdot \text{C} \cdot \text{CO} - \text{C} \cdot \text{CH} : \text{CH} \\ \parallel \quad \parallel \\ \text{N} - \text{NH} \end{array}$ , is prepared by boiling a slightly acidified aqueous solution of dihydrazinoanthraquinone hydrochloride, when the product separates in graphitic crystals. The *dipyrzole* derivative,

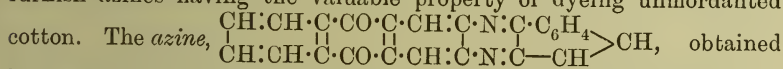




is formed when 1:5-disulphohydrazinoanthraquinone is heated at 140° with 3—5 per cent. hydrochloric acid. The product separates as its crystalline hydrochloride, and the base, which, when first set free, is amorphous, gradually assumes a crystalline form and is soluble in dilute aqueous sodium hydroxide to a yellow solution with a green fluorescence. Its solution in concentrated sulphuric acid is colourless, but has an intense blue fluorescence.

G. T. M.

**Preparation of Azines of the Anthraquinone Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 170562).—The *o*-diamines of the anthraquinone series, when condensed with *o*-diketones, furnish azines having the valuable property of dyeing unmordanted cotton. The *azine*,



by condensing 2:3-diaminoanthraquinone and  $\beta$ -naphthaquinone in boiling glacial acetic acid, separates in needles and in the reducing vat produces yellow shades on cotton. Similar *azines* were produced from 2:3-diaminoanthraquinone with phenanthraquinone,  $\beta$ -anthraquinone, and the oxidation product of alizarin-blue. 1:2-Diaminoanthraquinone also gives rise to an azine with  $\beta$ -naphthaquinone, whilst two products are obtained on condensing it with  $\beta$ -anthraquinone.

G. T. M.

**Constitution of *iso*Rosindone and Allied Substances.** HERMAN DECKER and AUGUST WÜRSCH (*Ber.*, 1906, 39, 2653—2656).—The inactivity of *isorosindone* towards magnesium phenyl bromide is an argument in favour of the phenolbetaine formula. The substance is unimolecular in benzene solution.

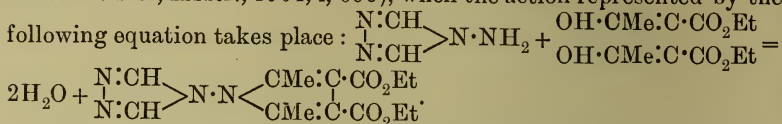
C. S.

**1-Amino-3:4-triazole (*N*-Amino- $\beta\beta'$ -pyrrodiazole).** A Contribution to the Knowledge of the so-called "*N*-Dihydro-tetrazine" (*iso*Bisdiazomethane, Trimethinetriazoimide). CARL BÜLOW (*Ber.*, 1906, 39, 2618—2622).—The compound described by Curtius and Lang as trimethinetriazoimide and by Hantzsch and Silberrad as dihydrotetrazine,  $\text{CH} \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{N} \cdot \text{NH} \end{smallmatrix} \text{CH}$ , is considered by the

author to be 1-amino-3:4-triazole,  $\text{NH}_2 \cdot \text{N} \begin{smallmatrix} \text{CH} \cdot \text{N} \\ \text{CH} \cdot \text{N} \end{smallmatrix}$ . The behaviour of

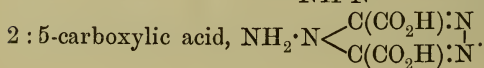
the compound was not in satisfactory accord with the formulæ advanced by previous authors. The new formula, however, is not contradictory to the fact that the compound yields a monoacetyl derivative only and not a diacetyl one, since it would be expected that the salts formed would undergo hydrolysis. Again, the formula accords with the formation of a 1:3:4-triazole by the action of nitrous acid. Further, the formation of condensation products with aldehydes is readily accounted for.

A direct proof that the so-called dihydrotetrazine is in reality 1-amino-3:4-triazole is afforded by its comportment with ethyl diacetylsuccinate (compare Bülow, Abstr., 1903, i, 196; Bülow and Sautermeister, Abstr., 1904, i, 690), when the action represented by the



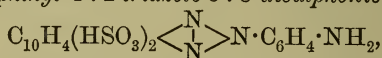
*Ethyl 1:1-triazole-2:5-dimethylpyrrole-3:4-dicarboxylate*, prepared in the manner indicated, crystallises from water in needles and melts at 146—147°.

It follows that Hantzsch and Silberrad's *N*-dihydrotetrazinedicarboxylic acid,  $\text{CO}_2\text{H} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{NH} \\ \text{NH} \cdot \text{N} \end{array} \text{C} \cdot \text{CO}_2\text{H}$ , is 1-amino-3:4-triazole-



A. McK.

[*p*-Aminophenylnaphthyl-1:2-triazole-3:8-disulphonic Acid.]  
AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 170513).—*p*-Aminophenylnaphthyl-1:2-triazole-3:8-disulphonic acid,



is obtained by successively condensing  $\alpha$ -naphthylamine-3:8-sulphonic acid with diazotised *p*-nitroaniline, oxidising the azo-compound thus formed to the corresponding nitrotriazole derivative, and then reducing the nitro-group with acid or alkaline reducing agents.

This aminotriazolesulphonic acid, when diazotised and combined with  $\beta$ -naphthol-3:6-disulphonic acid, furnishes a useful violet, lake-forming azo-derivative.

G. T. M.

**Diazobenzene Perchlorate and Phenylacridine Perchlorate**  
DANIEL VORLÄNDER (*Ber.*, 1906, 39, 2713—2715).—10-Phenylacridine dissolved in dilute 2—3 per cent. sulphuric acid gives with a dilute solution of perchloric acid (1 in 100) a voluminous precipitate of phenylacridine perchlorate consisting of slender, yellow needles. With a more dilute solution (1 in 1000) a turbidity is first produced, and then long, yellow needles separate. Chloric and hypochlorous acids do not yield precipitates except in more concentrated solutions. The test for perchloric acid is not conclusive, since a few acids, nitric acid in particular, form sparingly soluble salts of phenylacridine.

*Diazobenzene perchlorate*,  $\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{ClO}_4$ , separates in white needles when aniline is diazotised in perchloric acid solution, or when a 10 per cent. solution of diazobenzene chloride is treated with perchloric acid. It explodes even in the wet state, but remains white in the cold for one day.

The diazonium perchlorates obtained from *p*-toluidine, *p*-nitroaniline, *o*-, *m*-, and *p*-chloroaniline, *p*-bromoaniline, *o*-, *m*-, and *p*-aminobenzoic acid, *o*- and *p*-anisidine, and benzidine have been prepared. The para-compounds are the least unstable.

C. S.

**Diazonium Perchlorates.** KARL A. HOFMANN and H. ARNOLDI (*Ber.*, 1906, 39, 3146—3148).—*Diazobenzene perchlorate*,  $C_6H_5 \cdot N_2 \cdot ClO_4$ , prepared by diazotising an aqueous solution of aniline in a mixture of hydrochloric and perchloric acids, is sparingly soluble in water and is a very violent explosive. Compounds with similar explosive properties were obtained from *o*-toluidine, *p*-toluidine,  $\alpha$ -naphthylamine, and  $\beta$ -naphthylamine respectively  
A. McK.

**Preparation of Diazo-oxynaphthalenesulphonic Acids and their Anhydrides.** ANILINFARBEN- & EXTRACT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 171024).—The *o*-aminonaphthols and their sulphonic acids are not readily diazotised by the ordinary process, oxidation occurs, and  $\beta$ -naphthaquinone derivatives may be formed. This result occurs to some extent even in the absence of mineral acid, and is increased on warming the solution. It has now been ascertained that the addition of a comparatively small amount of a cupric salt renders the diazotisation of the aminonaphtholsulphonic acid complete even in the absence of mineral acid, and at the same time reduces the oxidising action to a minimum. To a well-cooled thin paste of 1-amino- $\beta$ -naphthol-4-sulphonic acid were added successively cold concentrated solutions of copper sulphate and sodium nitrite. The diazotisation proceeded quite smoothly, the product being soluble and yielding an orange-yellow solution from which 1-diazo-2-oxynaphthalene-4-sulphonic acid,  $HSO_3 \cdot C_{10}H_5 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ O \end{smallmatrix}_2$ , separated in fine yellow needles on the addition of concentrated hydrochloric acid. This diazo-compound, which is not explosive when dry, combines with resorcinol to furnish a dark violet azo-derivative.

*Barium-1-diazo-2-oxynaphthalene-6-sulphonate* was obtained as a golden-yellow, crystalline precipitate on adding successively copper chloride, sodium nitrite, hydrochloric acid, and barium chloride to a cold aqueous solution of 1-amino- $\beta$ -naphthol-6-sulphonic acid. *Barium-1-diazo-2-oxynaphthalene-7-sulphonate*, a light brown, crystalline substance, was prepared in a similar manner.

*1-Diazo-2-oxynaphthalene-8-sulphonic acid*, produced from the corresponding 1-amino- $\beta$ -naphthol-8-sulphonic acid, separates in colourless needles with a silvery lustre; this substance condenses with the phenols only with some difficulty; in the case of alkaline resorcinol, the solution has to be strongly heated.

The diazo-oxides of the 1-amino- $\beta$ -naphtholdisulphonic acids were also prepared through the agency of a cupric salt, and were isolated either as alkali or barium salts, and 1-diazo-2-oxynaphthalene-3:6:8-trisulphonic acid was obtained in the form of its crystalline, orange-yellow acid sodium salt.

In some cases a ferrous salt was employed instead of the copper compound. The mono-, di-, and tri-sulphonic acids of 2-amino- $\alpha$ -naphthol were also diazotised in this way, and were usually isolated in the form of the crystalline, yellow sodium salts. The patent contains a tabulated description of seventeen new diazo-oxynaphthalene sulphonic acids.

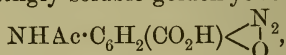
G. T. M.



Preparation of the Anhydrides of 1-Diazo-2-hydroxy- and 2-Diazo-1-hydroxy-naphthalenes. ANILINFARBEN- & EXTRACT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 172446. Compare preceding abstract).—1-Amino- $\beta$ -naphthol and 2-amino- $\alpha$ -naphthol can both be readily diazotised by treating the aqueous solutions of their hydrochlorides with a dilute solution of sodium nitrite and copper sulphate.

1-Diazo-2-oxynaphthalene,  $C_{10}H_6\begin{smallmatrix} N \\ | \\ O \end{smallmatrix}^2$ , is precipitated in yellow crystals on the addition of sodium chloride, whilst the crude 2-diazo-1-oxynaphthalene separates in yellowish-green crystals which are redissolved in the solution at  $80^\circ$ , and reprecipitated in yellow crystals on cooling. These compounds are very sensitive to light, darkening rapidly even in diffused daylight. G. T. M.

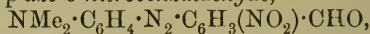
Azo-derivatives of 3-Amino-5-acetylaminosalicylic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 170819).—3-Amino-5-acetylaminosalicylic acid,  $OH\cdot C_6H_2(NH_2)(NHAc)\cdot CO_2H$ , which is obtained by successively nitrating and reducing acetyl-*p*-aminosalicylic acid, yields on diazotisation a sparingly soluble golden-yellow diazo-derivative,



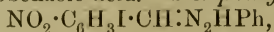
which combines with the sulphonic acids of the naphthols and dihydroxynaphthalenes to furnish a series of valuable mordant dyeing colouring matter G. T. M.

*para*-Substituted *o*-Nitrobenzaldehydes. V. FRANZ SACHS and HERMANN KANTOROWICZ (*Ber.*, 1906, 39, 2754—2762. Compare Abstr., 1902, i, 377, 682; 1903, i, 425; 1904, i, 62, 506, 593; 1905, i, 202; this vol., i, 575).—2-Nitrobenzaldehyde-4-diazonium sulphate,  $CHO\cdot C_6H_3(NO_2)\cdot N_2\cdot SO_4H$ , obtained by the action of amyl nitrite and sulphuric acid on 2-nitro-4-aminobenzaldoxime, is a pale yellow solid, readily soluble in water, but insoluble in most organic solvents, and decomposes when exposed to the air. The corresponding chloride,  $C_7H_4O_3N_3Cl$ , is more explosive and also more reactive.

Dimethylaniline-*p*-azo-*o*-nitrobenzaldehyde,



obtained by coupling the chloride with an acetic acid solution of dimethylaniline, crystallises in bordeaux-red, glistening plates and melts at  $219$ — $220^\circ$ . It dissolves readily in most organic solvents, but only sparingly in water, and readily dyes silk or wool. The *phenylhydrazone* gives a deeper shade of colour and is faster. Naphthol-*p*-azo-*o*-nitrobenzaldehyde,  $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_3(NO_2)\cdot CHO$ , crystallises from acetic acid, melts at  $208^\circ$ , and is only sparingly soluble in water. Phenol-*p*-azo-*o*-nitrobenzaldehyde,  $OH\cdot C_6H_4\cdot N_2\cdot C_6H_3(NO_2)\cdot CHO$ , melts at  $162^\circ$ , dyes wool or silk rose-red, and yields a *phenylhydrazone*. 4-Iodo-2-nitrobenzaldehyde,  $NO_2\cdot C_6H_3I\cdot CHO$ , melts at  $112^\circ$  and resembles the corresponding chloro- and bromo-compounds, but is far less stable, and, after exposure to sunlight for several hours is transformed into idonitrosobenzoic acid. The *phenylhydrazone*,

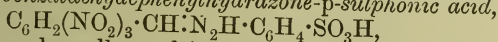


crystallises from alcohol in red needles melting at  $185^{\circ}$ , and the *semicarbazone*,  $C_8H_7O_3N_4I$ , from acetic acid in pale yellow, rectangular plates, which melt and decompose at  $284^{\circ}$ .

*2-Nitro-4-hydroxybenzaldehyde*,  $NO_2 \cdot C_6H_3(OH) \cdot CHO$ , obtained by decomposing the diazonium salts, crystallises from alcohol in yellow needles melting at  $67^{\circ}$  and has an intense odour. The *phenylhydrazone*,  $C_{13}H_{11}O_3N_3$ , forms glistening, red needles and melts at  $189-190^{\circ}$ .

*2:4-Dinitrobenzaldehyde-p-bromophenylhydrazone* forms red crystals melting at  $226-227^{\circ}$ , and its alcoholic solution gives a characteristic blue colour on the addition of a drop of potassium hydroxide solution. The corresponding *phenylmethylhydrazone*,  $C_{14}H_{12}O_4N_4$ , forms purple-red crystals melting at  $194^{\circ}$ .

*2:4:6-Trinitrobenzaldehyde-p-bromophenylhydrazone*,  $C_{13}H_8O_6N_5Br$ , crystallises from acetic acid in glistening, reddish-brown prisms melting at  $242^{\circ}$ . *Trinitrobenzaldehydephenylhydrazone-p-sulphonic acid*,



crystallises in pale red needles melting at  $211^{\circ}$ . It dissolves in alcohol and also in hot water, the aqueous solution giving brilliant but unstable colours with potassium hydroxide. Trinitrobenzaldehyde combines with sodium hydrogen sulphite and also yields a *semicarbazone*,  $C_8H_6O_7N_6$ , in the form of pale yellow plates melting at  $214^{\circ}$ . *Trinitrobenzylidenbenzidine*,  $C_6H_2(NO_2)_3 \cdot CH:N \cdot C_{12}H_8 \cdot NH_2$ , crystallises from xylene or amyl alcohol in glistening, blood-red plates melting at  $223^{\circ}$  and readily soluble in acetone or nitrobenzene. *Trinitrobenzylideneaniline*,  $C_{13}H_8O_6N_4$ , crystallises in pale yellow needles melting at  $162^{\circ}$ .

When reduced with alcoholic ammonium sulphide, the trinitrobenzaldehyde yields an extremely unstable pale yellow compound.

*2:6-Dinitro-4-aminobenzaldehydephenylhydrazone*,  $C_{13}H_{11}O_4N_5$ , obtained by the action of phenylhydrazine on the oxime, melts at  $250^{\circ}$ .

*2:6-Dinitrobenzaldehyde-4-diazonium chloride*,  $C_7H_3O_5N_4Cl$ , is readily soluble in water, and explodes violently when heated. The azo-derivatives of *o*-nitrobenzaldehyde do not yield indigo dyes with acetone and alkali.

J. J. S.

**Azo-colouring Matters of the Pyridine Series.** R. BAUMERT (*Ber.*, 1906, 39, 2971—2976).—Azo-colouring matters containing the pyridine ring have not hitherto been obtained, but by diazotising *p*-amino-4-stilbazole and *p*-amino-2-stilbazole, and coupling the products with phenols and amines, compounds of this kind have now been obtained.

*p-Nitro-4-stilbazole*,  $C_5NH_4 \cdot CH:CH \cdot C_6H_4 \cdot NO_2$ , prepared by heating approximately equal weights of  $\gamma$ -picoline, *p*-nitrobenzaldehyde, and freshly melted zinc chloride for nine hours at  $150-160^{\circ}$ , was obtained in the form of brown crusts after removing unaltered  $\gamma$ -picoline by distillation in steam; it forms yellow needles melting at  $118-119^{\circ}$ , is almost insoluble in water, and dissolves readily in organic media. Its crystalline *hydrochloride* melts at  $257-258^{\circ}$ ; the *platini-* and *aurochlorides* are also crystalline.

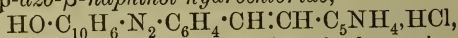
*p-Amino-2-stilbazole*, obtained by reducing *p*-nitro-2-stilbazole, crystallises from dilute alcohol in pale yellow needles melting at  $138-139^{\circ}$ ;

its *stannochloride*,  $C_{13}H_{14}N_2Cl_2 \cdot 2SnCl_2$ , obtained during the reduction, melts at  $198-199^\circ$ ; the *platinichloride* forms yellow needles.

*Di-2-stilbazylthiocarbamide*,  $C_{27}H_{22}N_4S$ , which results from the condensation of *p*-amino-2-stilbazole and carbon disulphide in alcoholic potash, melts at  $180-181^\circ$  and forms a yellow *platinichloride*,  $C_{27}H_{22}N_4S(H_2PtCl_6)_2$ . *Acetyl-p-amino-2-stilbazole*,  $C_{15}H_{14}ON_2$ , crystallises from dilute alcohol in slender needles and melts at  $170-171^\circ$ .

*p*-Amino-4-stilbazole, prepared by reducing *p*-nitro-4-stilbazole, melts at  $138-139^\circ$ ; its *hydrochloride* and *stannochloride*,  $C_{13}H_{14}N_2Cl_2 \cdot 2SnCl_2$ , melt at  $257-258^\circ$  and  $198-199^\circ$  respectively; the *platinichloride* melts above  $300^\circ$ . The *thiocarbamide* derivative melts at  $195-196^\circ$ ; its *platinichloride* melts above  $300^\circ$ .

*2-Stilbazole-p-azo-β-naphthol hydrochloride*,

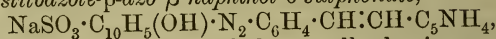


was obtained by adding a solution of diazotised *p*-amino-2-stilbazole to alkaline  $\beta$ -naphthol and subsequently acidifying the solution of the azo-compound. This salt, which crystallises from 90 per cent. alcohol in reddish-brown leaflets, melts at  $252-253^\circ$  and dyes silk, wool, and ordinary and mordanted cotton; it is only slightly soluble in water, and, like benzeneazo- $\beta$ -naphthol, is devoid of phenolic properties, being insoluble in aqueous alkali hydroxides.

*4-Stilbazole-p-azo-β-naphthol hydrochloride* resembles its isomeride, but dyes in somewhat deeper shades and melts at  $257-258^\circ$ .

The hydrochlorides of *2-stilbazole-p-azoresorcinol* and *4-stilbazole-p-azoresorcinol* are brown powders sparingly soluble in water, more so in alcohol, and dissolving in aqueous alkali hydroxides.

*Sodium 2-stilbazole-p-azo-β-naphthol-6-sulphonate*,



crystallises from 90 per cent. alcohol in needles having a green, metallic lustre; its isomeride from diazo-4-stilbazole has similar properties. Similar dyes can be obtained from the two isomeric diazostilbazoles with  $\beta$ -naphthol-3:6-disulphonic acid and also with  $\beta$ -naphthol-6:8-disulphonic acid, salicylic acid, dimethylaniline, and sulphanic acid.

G. T. M.

**Tertiary Aromatic Amines. V.** CARL HAEUSSERMANN (*Ber.*, 1906, 39, 2762—2765).—*Tetraphenyldiaminoazobenzene*,  $C_{36}H_{28}N_4$ , is obtained when nitrotriphenylamine is reduced electrolytically. The best results are obtained when the cathode compartment contains an alcoholic solution of the nitro-compound and sodium acetate, the anode compartment an aqueous solution of sodium hydroxide, and the electrodes are of nickel gauze or platinum.

The azo-compound separates from benzene as orange-red crystals melting at  $201-202.5^\circ$ , and is only sparingly soluble in alcohol or acetone.

*Aminotriphenylamine* (Herz, *Abstr.*, 1890, 1409), obtained by the action of ammonia on its hydrochloride, crystallises from ether or alcohol in glistening, colourless needles melting at  $146-147.5^\circ$  and distilling above  $360^\circ$ .

Triphenylamine does not readily condense with diazobenzene chloride, whereas diphenyl-*m*-toluidine reacts with an acetic acid



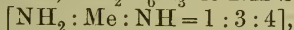
solution of diazobenzene chloride, yielding *benzeneazodiphenyl-m-toluidine*,  $C_{25}H_{21}N_3$ , which, after repeated crystallisation from acetone, forms scarlet-red needles melting at 168—169°. It is readily soluble in benzene, but less so in alcohol.

Triphenylamine and benzaldehyde condense in the presence of 50 per cent. sulphuric acid, yielding a pale green product which, after extraction with alcohol, is colourless. It probably consists of tetraphenyldiaminotriphenylmethane.

J. J. S.

### Azimino-compounds from Aromatic *para*-Diamines.

GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT (*Ber.*, 1906, 39, 2869—2875. Compare *Trans.*, 1905, 87, 73; 1906, 89, 1158).—*p*-Toluenesulphonyl-5-nitro-*o*-toluidine (Reverdin and Crépieux, *Abstr.*, 1902, i, 238, 434) may be obtained by the action of *p*-toluenesulphonic chloride on a boiling toluene solution of 5-nitro-*o*-toluidine; when reduced with iron filings and dilute acetic acid, it yields *p*-toluenesulphonyl-*p*-toluenyldiamine,  $NH_2 \cdot C_6H_3Me \cdot NH \cdot SO_2 \cdot C_7H_7$



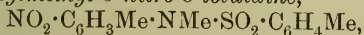
which crystallises from dilute alcohol in slender prisms melting at 150°. When the diazonium chloride derived from the base is mixed with excess of sodium acetate solution, it yields *p*-toluenesulphonyl-*p*-

aziminotoluene,  $C_6H_3Me \cdot \begin{smallmatrix} N \cdot SO_2 \cdot C_7H_7 \\ | \\ N_2 \end{smallmatrix}$ ; this is practically insoluble in

the usual organic solvents, but dissolves sparingly in hot pyridine, naphthalene, or *p*-toluidine. It has a pale yellow colour and decomposes violently at 156°. The azimino-compound is converted back into the diazonium salt by cold concentrated hydrochloric acid and then condenses with  $\beta$ -naphthol, yielding 2-*p*-toluenesulphonylaminotoluene-5-azo- $\beta$ -naphthol,  $OH \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_3Me \cdot NH \cdot SO_2 \cdot C_7H_7$ , which crystallises from benzene or acetic acid in glistening, red needles melting at 194°.

The same azo-compound can be obtained by heating equivalent quantities of the azimino-compound and  $\beta$ -naphthol in dry pyridine.

*p*-Toluenesulphonylmethyl-5-nitro-*o*-toluidine,



obtained by heating Reverdin and Crépieux's nitro-compound with methyl iodide and alkali in methyl-alcoholic solution, melts at 103—105°. When reduced it yields *p*-toluenesulphonylmethyl-*p*-toluenediamine,  $NH_2 \cdot C_6H_3Me \cdot NMe \cdot SO_2 \cdot C_7H_7$ , which crystallises in colourless plates melting at 118—119°; the corresponding diazonium salt does not yield an azimino-compound with sodium acetate, but couples with  $\beta$ -naphthol to an azo-dye,  $C_{25}H_{23}O_3N_3S$ , which separates from acetic acid in deep red, nodular crystals melting at 181°.

J. J. S.

### Condensation of Diazobenzeneimides with Pyrazolones.

REINHOLD VON WALTHER and P. ROTHACKER (*J. pr. Chem.*, 1906, [ii], 4, 207—208. Compare Dimroth, *Abstr.*, 1902, i, 403).—The action of various diazobenzeneimides on phenylmethylpyrazolone in presence of sodium ethoxide leads to the formation of a red product, which is formed also in small quantities by the interaction of 4-dichloropyrazolone, pyrazolone, and hydrazine. It melts at 184°, is insoluble

in water, only sparingly so in organic solvents, is readily soluble in hot dilute alkali hydroxides or concentrated sulphuric or hydrochloric acid, and forms two series of salts, of which the acid series is yellowish- to blood-red, whilst the normal salts are yellow, and are readily soluble in water, alcohol, or ether; the *platinichloride* can be extracted from its aqueous solution by shaking with ether. The *acetyl* derivative is yellow to dark red, the *diacetyl* derivative is yellow. The decomposition of the product melting at  $184^{\circ}$  leads to the formation on the one hand of rubazonic acid and bispyrazolone, and on the other of hydrazine; it contains probably 2 mols. of the pyrazolone coupled by means of a hydrazine group.

1-Phenyl-3:4-dimethylpyrazolone does not react with diazobenzene-imide. G. Y.

**Production of Colloidal Preparations containing Gold, Silver, or Copper.** KALLE & Co. (D.R.-P. 170433, 170434).—Colloidal substances containing silver or gold are obtained by adding silver nitrate or gold chloride to an alkaline solution of the alkali salts of the fission products of albumin (lysalbuminates, protoalbuminates, alkali albumoses, &c.), warming gently for some time, and then dialysing the solution. The colloidal solution thus obtained yields a precipitate with dilute acid which may be again dissolved in alkali and purified by repeated dialysis.

An alkaline solution containing sodium protoalbuminate, sodium hydroxide, and copper sulphate, when dialysed until the diffusate was neutral and then evaporated on the water-bath, furnished a brownish-black powder containing 18—19 per cent. of copper, which dissolves in water and aqueous sodium hydroxide to brown and violet solutions respectively. The other fission products of albumin gave rise to similar copper compounds. G. T. M.

**Equilibrium between Proteids and Electrolytes. III. Solubility of Globulin in Magnesium Sulphate: Influence of Temperature.** GINO GALEOTTI (*Zeit. physiol. Chem.*, 1906, 48, 473—480. Compare Abstr., 1905, ii, 512).—The more concentrated a solution of magnesium sulphate is, the more serum-globulin does it dissolve. When the concentration approaches saturation, the globulin is precipitated, and this precipitation depends on the concentration. The term fractional globulin precipitation should not be used if that expression means that the globulins in the fractions are distinct substances. An increase of temperature increases the solubility of the globulin in dilute solutions of the salt, but lessens it in concentrated solutions. W. D. H.

**Hydrolysis of Vitellin.** EMIL AEDERHOLDEN and ANDREW HUNTER (*Zeit. physiol. Chem.*, 1906, 48, 505—512).—The following figures relate to the monoamino-acids of vitellin from egg yolk, compared with those similarly obtained by hydrolysis from the closely related proteid caseinogen of cow's milk. The numbers given are percentages.

	Vitellin.	Caseinogen.
Glycine .....	1.1	0
Alanine .....	present	0.9
Aminovaleric acid .....	2.4	1.0
Leucine .....	11.0	10.5
Aspartic acid.....	0.5	1.2
Glutamic acid.....	12.2	11.0
Phenylalanine .....	2.8	3.2
Proline .....	3.3	3.1
Serine .....	—	0.23
Tyrosine.....	1.6	4.5

W. D. H.

**Cleavage Products of Vitellin.** PHOEBUS A. LEVENE and C. L. ALSBERG (*J. Biol. Chem.*, 1906, 2, 127—133)—One hundred grams of vitellin yield, glycine, traces; alanine, 0.16; leucine, 3.3; proline, 4; aspartic acid, 0.6; glutamic acid, 1; phenylalanine, 1; tyrosine, 0.4; histidine, traces; arginine, 1.2; and lysine, 2.4. The high proportion of proline [pyrrolidine-2-carboxylic acid] is significant in view of the fact that vitellin furnishes the material for the production of hæmoglobin.

W. D. H.

**Deaminocasein.** ZDENKO H. SKRAUP and PH. HOERNES (*Monatsh.*, 1906, 27, 631—652. Compare Paal, *Abstr.*, 1896, i, 455; Schiff, *ibid.*, 632; Schroetter, *Abstr.*, 1898, i, 610).—The action of sodium nitrite on casein dissolved in glacial acetic acid at the ordinary temperature and finally on the water-bath leads to the formation of *deaminocasein*,  $C_{216}H_{349}O_{78}N_{54}SP_{0.4}$ ; it is obtained as a light yellowish-brown substance, does not give Millon's or the biuret reaction, is much less soluble than is casein in aqueous alkali hydroxides or acids, gives Liebermann's nitroso-reaction, and forms a brown, gelatinous *sodium* derivative. When hydrolysed with boiling 36 per cent. sulphuric acid it yields oxalic acid; the product of the hydrolysis with fuming hydrochloric acid, when treated according to Fischer's method (*Abstr.*, 1901, i, 780), is found to contain leucine, aminovaleric acid, pyrrolidine-2-carboxylic acid, and probably glycine and *isoleucine*; glutamic, caseic, and caseanic acids are present in about the same amounts as, but arginine in much smaller quantity than, in the hydrolysis products of casein. Lysine and tyrosine are not present, whilst the presence of alanine is doubtful.

When boiled with dilute sulphuric acid, casein yields 1.38, deaminocasin 1.77 per cent. of ammonia.

G. Y.

**Deaminoglutin.** ZDENKO H. SKRAUP (*Monatsh.*, 1906, 27, 653—662. Compare Skraup and Hoernes, preceding abstract).—*Deaminoglutin*,  $C_{1039}H_{1669}O_{391}N_{297}S$  or, omitting consideration of the sulphur,  $C_{3.51}H_{5.71}O_{1.32}N$  (glutin,  $C_{3.23}H_{5.31}O_{1.27}N$ ), is prepared by treating gelatin with sodium nitrite in acetic acid solution; it forms a light brownish-yellow resin, is readily soluble in water, less so in alcohol, gives a reddish-violet biuret reaction, and when hydrolysed by means of fuming hydrochloric acid on the water-bath, forms a fluorescent



solution. The product of hydrolysis contains oxalic acid, glycine, histidine, and arginine. Lysine, which is present as a product of the hydrolysis of glutin, is not obtained from deaminoglutin; in its place there is found a *picrate* which melts at 149–150° and yields a product melting at about 220°, together with a hydroxyaminovaleric acid crystallising in leaflets, and melting at 252°. The *picrate* formed from this gives analytical results agreeing best with those required by the picrate of an aminovaleric acid,  $C_{11}H_{14}O_9N_4$ . G. Y.

**Monoamino-acids of Gluten.** EMIL ABDERHALDEN and FERNAND MALENGREAU (*Zeit. physiol. Chem.*, 1906, 48, 513–518).—The following figures are the percentages of amino-acids obtained from gliadin, the proteid of gluten of wheat which is soluble in alcohol, compared with those from gluten (or gluten-casein) which is insoluble in that reagent.

	Gluten.	Gliadin.
Glycine .....	0.41	0.68
Alanine .....	0.3	2.66
Aminovaleric acid .....	not found	0.33
Leucine .....	4.1	6.0
Proline .....	3.97	2.4
Glutamic acid .....	24.0	31.5
Aspartic acid.....	0.64	1.24
Phenylalanine .....	1.0	2.6
Tyrosine.....	1.9	2.37
Tryptophan .....	{ not estimated.	1.0 (approx.)
Serine .....		0.12
Lysine .....	2.15	0.0
Histidine .....	1.16	1.2
Arginine .....	4.4	2.75

W. D. H.

**Formation of Methæmoglobin. II.** ALLEXIS BABEL (*Arch. Sci. phys. nat.*, 1906, [iv], 22, 216–239).—The substances (compare this vol., i, 779) which convert oxyhæmoglobin into methæmoglobin are not acting as catalytic agents, because if care is taken to avoid secondary reactions it is not possible to recover the whole of the substance at the end of the reaction; and, further, there exists for each substance a limiting quantity below which it is incapable of effecting any change in the oxyhæmoglobin. It is probable that in the conversion of oxyhæmoglobin into methæmoglobin, hæmoglobin is formed as an intermediate product; this undergoes a molecular rearrangement owing to the toxic action of the reacting substance, and is then oxidised to methæmoglobin. M. A. W.

**Oxyhæmoglobin Fluorides.** ANTONY VILA and M. PIETTRE (*Bull. Soc. chim.*, 1906, [iii], 35, 685–688. Compare Abstr., 1905, i, 847).—The first portion of the paper is polemical against Ville and Derrien (Abstr., 1905, i, 399, 500, 622), and affirms the views put forward in the authors' previous papers (Abstr., 1905, i, 399, 500,

622, 847 ; ii, 402). In the second portion it is shown that the shifting of the new absorption band of oxyhæmoglobin from  $\lambda 612$  to  $\lambda 634$ , brought about by the addition of minute quantities of fluorides, may be used for the detection of the latter (compare Ville and Derrien, this vol., ii, 390). The optical effect is even shown when oxyhæmoglobin is added to water in which such insoluble fluorides as those of calcium, barium, or strontium have been suspended. The simultaneous presence of phosphates, however, diminishes the sensibility of this test in the case of soluble fluorides, and may completely mask it in the case of the slightly soluble fluorides. Thus fluorine cannot be detected in bone ash, teeth ash, or apatite by this method.

T. A. H.

**Oxidation of Nucleic Acids. I.** HANS STEUDEL (*Zeit. physiol. Chem.*, 1906, 48, 425—429).—When copper nucleate is mixed with concentrated nitric acid, a vigorous action ensues ; a similar reaction, but less violent, occurs when the nitric acid is previously diluted with its own volume of water. After several days a considerable precipitate of guanine and adenine nitrates is formed. Other products of oxidation are xanthine, hypoxanthine, thymine, uracil, and oxalic acid, products which, with the exception of oxalic acid, are also formed by the hydrolytic decomposition of nucleic acid. Pure adenine gives neither Millon's reaction nor the red coloration with diazobenzene salts in alkaline solution.

J. J. S.

**Lecithin-sugar and Jecorin and the Physico-chemical Behaviour of Sugar in the Blood.** PAUL MAYER (*Chem. Centr.*, 1906, ii, 536—537 ; from *Biochem. Zeit.*, 1906, 1, 81—107).—Lecithin-dextrose is probably a solid solution or a molecular combination of the two substances. Aqueous solutions of the substance are precipitated by sodium chloride, barium chloride, or silver nitrate. Lecithin-dextrose readily reduces an alkaline solution of copper, is fermentable, and forms an *osazone* which melts at  $205^{\circ}$ . Jecorin and lecithin-dextrose are not identical, because the sugar is firmly attached in the former compound and only loosely in the latter. The existence of a ferment in the blood which is able to split off sugar from jecorin is denied ; it is, moreover, improbable that sugar occurs in the blood combined in the form of jecorin. A physiological salt solution of jecorin activates cobra poison in just the same way as lecithin.

P. H.

**The Rendering Insoluble of Gelatin by Oxidation Products of Phenols.** AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 600—602).—In addition to the developers already studied (this vol., i, 614) it is found that the phenols, gallic acid, gallotannic acid,  $\alpha$ -naphthol,  $\beta$ -naphthol, resorcinol, phloroglucinol and dihydroxynaphthalene possess the property of rendering gelatin insoluble in presence of air and sodium carbonate. The rapidity with which these substances render gelatin insoluble is proportional to the readiness with which they oxidise on exposure to air in alkaline solution.

T. A. H.

**Action of Alums and Aluminium Salts on Gelatin.** AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 676—681).—Freshly-precipitated alumina and the various salts of aluminium possess the property of raising the "setting" temperature of gelatin solutions. This effect is due to the alumina, since different quantities of the various salts produce the same rise in the "setting" temperature so long as they yield the same quantity of alumina. The "setting" temperature increases proportionately with the quantity of aluminium salt until the equivalent of 0.64 gram of alumina per 100 grams of gelatin has been added. Further additions have at first no effect on the "setting" temperature, but finally cause it to fall. Gelatin is able to fix alumina, and when the latter is applied in the form of a salt, subsequent washing with water appears to dissociate the salt and remove the acid, leaving what is apparently a compound of gelatin and alumina in which the maximum possible amount of the latter present is 3.6 per cent. by weight.

T. A. H.

**Peptones from Casein.** ZDENKO H. SKRAUP and R. WITT (*Monatsh.*, 1906, 27, 663—684. Compare Skraup and Zwerger, this vol., i, 123; Kossel, *Abstr.*, 1902, i, 128; Siegfried, *Abstr.*, 1903, i, 586; 1904, i, 953; 1905, i, 104).—The authors have repeated the investigation of Siegfried's caseinokyrine, the isolation of the kyrine being carried out under the conditions described by Siegfried. The results obtained are similar to those of Skraup and Zwerger (*loc. cit.*). The phosphotungstate of the supposed kyrine, on being fractionally extracted with 80 per cent. alcohol, yields a series of salts of different solubilities, most of which are thrown down on addition of water; the alcoholic filtrates react with picric acid, forming lysine picrate. Siegfried's caseinokyrine sulphate is free lysine.

When dissolved in dilute acetic acid and hydrolysed with 12 per cent. hydrochloric acid, casein yields a laevorotatory solution which becomes less active, but not dextrorotatory, and contains two peptones. Of these, one is precipitated by potassium mercuric iodide, contains relatively much tyrosine, histidine 0.9, arginine 1.4, and lysine 2.2 per cent. The second is precipitated by picric acid, but not by potassium mercuric iodide, contains relatively little tyrosine, histidine 2.0, and lysine 3.0 per cent., but no arginine. Both peptones give a red biuret reaction, and are precipitated from their solutions in dilute sulphuric acid on addition of a saturated solution of ammonium sulphate.

G. Y.

**Decomposition of Proteid.** MAX DENNSTEDT and F. HASSLER (*Zeit. physiol. Chem.*, 1906, 48, 489—504).—An unfinished piece of work on the primary hydrolytic products (proteoses and peptones) prepared from zein, the alcohol-soluble proteid of maize. The authors' view is that the formation of such substances is not due to simple hydrolysis, but that there is also oxidation leading to the splitting off of some of the nitrogen as ammonia, and some of the sulphur as hydrogen sulphide.

W. D. H.



**Influence of Light on Ferments (Invertase) in the Absence of Oxygen.** A. JODLBAUER and HERMANN VON TAPPEINER (*Chem., Centr.*, 1906, ii, 693; from *Münch. med. Woch.*, 53, 653).—The influence of sunlight on the action of invertase has been examined by operating in quartz vessels which transmit ultra-violet rays. The action is measurably retarded in an atmosphere of hydrogen, nitrogen, or carbon dioxide. The retarding influence of light is not increased in an atmosphere free from oxygen when fluorescent substances are added to the solution. This result is quite different from that obtained in the presence of oxygen; in this case, fluorescent substances increase the effect of illumination many times.

H. M. D.

**Diastase. I. Preparation and Properties.** SIGMUND FRÄNKEL and MAX HAMBURG (*Beitr. chem. Physiol. Path.*, 1906, 8, 389—398).—The diastatic power of the malt extract is determined, and then a clear solution of basic lead acetate is added so long as the diastatic power shows no appreciable diminution. After filtration, the clear liquid should not yield a precipitate with ammonium sulphide. The liquid is passed through a Pukal filter into sterilised flasks, and is inoculated with a pure culture of Froberg yeast, which has been previously grown in a medium rich in diastase and poor in sugar. After fermentation is completed, the liquid is drawn again through a Pukal filter into a sterilised vacuum apparatus, and is distilled under a pressure of 10 mm. until the volume is some 500 c.c. It is then fermented by a mixture of Froberg and Logos yeasts, again filtered, and evaporated under reduced pressure, when a syrup is obtained. When dried over sulphuric acid, this forms a powder which is free from reducing or fermentable sugars and also from albumins.

The precipitation of calcium phosphate or barium sulphate in a solution of pure diastase carries down only a minute portion of the enzyme; shaking with aluminium hydroxide has the same effect. The enzyme may be completely removed from solution by the addition of colloidal ferric hydroxide, but its activity appears to be destroyed at the same time.

During electrolysis, diastase does not collect around the anode or cathode; it is, however, a colloid, as has been proved by means of the ultra-microscope. The diastase appears to be a mixture of various enzymes, and when dialysed into spring water it is largely separated into sugar forming enzymes which pass into the water and liquefying enzymes which remain within the dialysing membrane. Many organic solvents, such as alcohol or acetone, rapidly destroy the activity of pure diastase.

J. J. S.

**Reversible Enzyme Action. Formation and Decomposition of Esters by Pancreatic Enzymes.** HENRI POTTEVIN (*Bull. Soc. chim.*, 1906, [iii], 35, 693—696).—Most of the facts recorded have been given already in *Abstr.*, 1903, ii, 439, 494; 1904, i, 284. It is now shown that under suitable conditions of temperature and concentration oleates of propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, and *tert*-butyl are produced by the action of the pancreatic ferment on mixtures of the appropriate alcohols with oleic acid.

T. A. H.

**Action of Emulsin on  $\beta$ -Glucosides.** HUGH RYAN and GEORGE EBRILL (*Proc. Roy. Irish Acad.*, 1906, 26, B, 53—55. Compare Abstr., 1904, i, 223).—The authors have tested the action of emulsin on  $\beta$ -o-tolyl arabinoside,  $\beta$ -carvacryl arabinoside,  $\beta\beta$ -naphthylarabinoside, and  $\beta$ -phenyl glucoside. The last compound was almost completely converted into phenol and dextrose, but in the case of the arabinosides, although faint odours of carvacrol and cresol were observed, there was no indication of even a trace of arabinose.

A table is given showing those synthetical glucosides which are hydrolysed and those which are not hydrolysed by emulsin. It is seen that the activity of emulsin towards a glucoside depends not only on the configuration of the molecule, as Fischer pointed out, but also on the nature of the groups. Thus the replacement of four hydrogen atoms in  $\beta\beta$ -naphthyl glucoside by four acetyl groups converts a glucoside hydrolysable by emulsin into one which cannot be so hydrolysed; the conversion of salicin into its benzoyl derivative, populin, has a similar effect.

T. H. P.

**Action of Lipase.** ALONZO E. TAYLOR (*J. Biol. Chem.*, 1906, 2, 87—104. Compare Kastle and Loevenhart, Abstr., 1901, i, 178; Kastle, Johnston, and Elove, *ibid.*, 1904, i, 702).—All the experiments have been made with the powder obtained by repeatedly extracting castor beans with dry ether and crushing. This powder contains lipase, amylase, invertase, maltase, and an endotrypsin, but not any peroxydase. It is possible to separate lipase from the other enzymes, but the product is then much less stable. With water it forms a cloudy emulsion, and when repeatedly filtered loses its activity. When dry it may be heated above 100° without injury. Its activity is not destroyed by free acid, but when heated with water the enzyme is hydrolysed. Its action on triacetin has been studied; it has a markedly accelerating effect on the hydrolysis. The reverse process, conversion of glycerol and acetic acid into triacetin, has a very low velocity and for all practical purposes may be neglected, although in the hydrolysis a state of equilibrium is established. This equilibrium mixture has practically the same composition as the mixture formed when acids are used in the hydrolysis.

The results obtained for the hydrolysis agree with those for a unimolecular reaction and the ratio  $Vt_n + 10^\circ / Vt_n = 2.6$  between 18° and 28°.

In the case of triolein, Henri and Nieloux's results (*Compt. rend. Soc. Biol.*, 1904, 67, 175) have been confirmed, namely, that  $t/x$  is constant. In this reaction the temperature coefficient is small, as an increase of 10° produces an increase of only some 20 per cent. in the velocity. The velocity measured in this case of a two-phase system is thought to be the diffusion velocity, and not the velocity of the chemical reaction.

J. J. S.

**Fission of Lipoid Substances by Lipase and the Optical Antipodes of Natural Lecithin.** PAUL MAYER (*Chem. Centr.*, 1906, ii, 493—494; from *Biochem. Zeit.*, 1906, 1, 39—52).—Lecithin, jecorin, and protagon are readily split up by lipase; the reaction takes place in

neutral solution, but less readily than in faintly acid solution. Gastric juice has no action on these substances. Ordinary dextrorotatory lecithin, when heated in a sealed tube with ten times the quantity of methyl alcohol for five or six hours at 90—100°, yields inactive lecithin in a form which is partly crystalline and partly pasty; this substance is soluble in alcohol, ether, light petroleum, or chloroform, and is only slightly soluble in acetone; when freshly prepared it is light yellow, but it soon darkens. *l-Lecithin*, which is obtained by the action of steapsin on inactive lecithin, has  $[\alpha]_D - 8.59^\circ$ . *d-Glycerophosphoric acid*, which is formed at the same time by the action of the lipase on the *d*-lecithin in the inactive mixture, forms white flakes and has  $[\alpha]_D - 1.04^\circ$ .  
P. H.

**Nature and Effects of Rennet Coagulation.** III. KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1906, 8, 365—369. Compare this vol., i, 127).—In the precipitation of cheese, free hydrogen ions are produced as in the precipitation of paracasein. The formation of cheese depends on both temperature and amount of calcium ion.

Pure casein is decomposed by rennin in a very short time, yielding albumoses. This proteolysis is not due to pepsin mixed with the rennin.  
J. J. S.

**Specific Action of Peroxydases as Enzymes.** ALEXIS BACH (*Ber.*, 1906, 39, 3329—3331. Compare this vol., i, 616).—A reply to Chodat's claim for priority (this vol., i, 779). The so-called Chodat-Bach theory was suggested simultaneously by Engler and Bach.

G. Y.

**Lactic Acid Fermentation.** EDUARD BUCHNER and JAKOB MEISENHEIMER (*Annalen*, 1906, 349, 125—139).—The amount of zinc lactate obtained, and not that of the carbon dioxide liberated from calcium carbonate, must be taken as the measure of the lactic acid formed by fermentation; 2.1 and 1.25 grams respectively of zinc lactate have been obtained by the action of 10 grams each of two further enzyme preparations from *Bacillus Delbrücki* (compare Abstr., 1903, ii, 318). The enzymes become ineffective if during the preparation the heating is carried out at 90—92° for one hour. In all experiments the bacteria were killed by treatment with toluene, the resulting preparations causing neither growth nor acidification in contact with sterilised tubers at 45° for eight weeks.

It may be now considered certain that the lactic acid fermentation of sugar is caused by the action of an enzyme, the lactic acid bacteriozymase, which is a product of the living lactic acid bacteria and can be separated from it; the lactic acid is decomposed in the second stage to carbon dioxide and alcohol by the lactacidase.

A series of experiments were made with the expressed juices of *Bacillus Delbrücki*; these were not capable of forming lactic acid from sugar, the fermentative agent remaining in the residue from the expression.

As the enzyme preparation from *Bacillus Delbrücki* ferments maltose as well as sucrose, the presence of a hydrolytic enzyme must be assumed. In both cases inactive lactic acid is formed.



A 10 per cent. solution of sucrose, when treated with the enzyme preparation at 35° for one hour, has a faint reducing action towards Fehling's solution.

As both *d*- and *l*-lactic acid have been obtained by treating maltose with the living bacillus, and *d*-lactic acid has been formed in the same manner from sucrose, it is evident that the nature of the product depends on some condition such as the length of time of the fermentation, the presence of calcium carbonate, or the nature of the culture medium. G. Y.

**Acetic Acid Fermentation.** EDUARD BUCHNER and RUFUS GAUNT (*Annalen*, 1906, 349, 140—184. Compare preceding abstract; Buchner and Meisenheimer, *Abstr.*, 1903, ii, 318).—The paper opens with an account of the work of previous authors on the acetic acid fermentation of alcohol.

The activity of nine separate enzyme preparations from beer-vinegar bacteria prepared by Buchner and Meisenheimer's method was tested. The comparative activity depends on the uniformity of the acetone treatment, the genesis of the culture, and the temperature at which the pure culture is grown on the tubers; 100 grams of the most active preparation, obtained from about 220 grams of the living bacteria containing 55 per cent. of water, produced 4 grams of acetic acid. Finely powdering the enzyme does not alter the oxidising effect. Active preparations, obtained when the centrifugalised, living bacteria were dried on a porous plate before being added to the acetone, were not sterile; sterility is produced only by adding the still moist bacteria to the acetone and treating the enzyme with toluene.

In two experiments, propyl alcohol was oxidised to propionic acid by the enzyme preparation from beer-vinegar bacteria. It may be regarded as certain that the acetic acid fermentation of alcohol is caused by an enzyme, to be called the alcohol-oxydase, which is a product of the vinegar bacillus. The ash of the bacteria contains an amount of iron equivalent to 0.08 per cent. of the enzyme preparation, which in alcoholic guaiacum resin solution gives a transient coloration with hydrogen peroxide.

The relation of the alcohol-oxydase to other known oxidising enzymes is discussed.

The expressed juice of the beer-vinegar bacteria does not oxidise alcohol in the presence of air (compare preceding abstract).

The results of the experiments described are given in a series of tables. G. Y.

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## Organic Chemistry.

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**Alkaline Aqueous Mercuri-iodide as a Reagent for Hydroxyl Groups.** LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1906, 244, 373—375).—When boiled for one minute with Nessler's solution, substances which contain a primary or a secondary alcohol group bring about a reduction of the solution (to metallic mercury). Substances containing a tertiary alcoholic group do not effect this reduction. The action of substances containing phenolic groups is varied.

Sachsse's (alkaline mercuri-iodide) solution reacts in the same way, but not Knapp's (alkaline mercuricyanide) solution. C. F. B.

**Preparation of Chemically Pure Methyl and Ethyl Alcohols; their Specific Gravities.** PETER KLASON and EVERT NORLIN (*Arkiv Kem. Min. Geol.*, 1906, 2, No. 24, 1—7).—Chemically pure methyl or ethyl alcohol may be prepared as follows: 500 grams of pure potassium methyl (or ethyl) sulphate are dissolved in water, and to the solution rather more than the calculated quantity of pure sulphuric acid is added, the whole liquid measuring about 2 litres. The methyl (or ethyl) alcohol is distilled in a current of steam and concentrated by fractionation, finally, from ignited potassium hydroxide. To remove the last traces of moisture, freshly ignited lime (from marble) and, finally, calcium are used. Distillation from calcium is continued until the specific gravity of the alcohol undergoes no further change.

Pure methyl alcohol has the sp. gr. 0.796472 at 15°/15°, and, between 0° and 30°, the sp. gr. at  $t^{\circ}/4^{\circ}$  is expressed by  $0.80999 - 0.00093 t - 0.00000025 t^2$ .

Pure ethyl alcohol has the sp. gr. 0.794130 at 15°/15°; the value 0.79429, on which Windisch's tables are calculated, indicates that the alcohol used by this author contained 0.05 per cent. of water. Its sp. gr. at 0°/4° is 0.80628; at 10°/4°, 0.79792; at 20°/4°, 0.78938; at 30°/4°, 0.78080. These values agree well with those obtained by Winkler.

T. H. P.

*sec.*- and *tert.*-Pinacolyl Alcohols and their Separation. MAURICE DELACRE (*Bull. Soc. chim.*, 1906, [iii], 35, 811—816. Compare this vol., i, 476, 518, 551, 784).—*tert.*-Pinacolyl alcohol was obtained by the application of the Grignard reaction to isopropyl bromide. Its odour is similar to that of the alcohol prepared from pinacolin, and after the removal of traces of impurity by shaking it with solid potassium hydroxide, it boils at 118.4—119.2° under 748 mm. pressure and freezes about 10.5°. The chloride boils from 112—113.4° and solidifies at 7°; the acetate, obtained by warming the alcohol with acetic anhydride for several hours, boils from 125—140°. When the alcohol is heated with the anhydride in a closed tube for three days at 200°, the principal product is tetramethylethylene

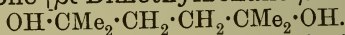
( $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene). The *tert*.-pinacolyl alcohol (and also the alcohol regenerated from the acetate described above) is dehydrated by dilute sulphuric acid much more rapidly than the alcohol obtained from pinacolin, and this method may be used for their separation.

The synthetic *tert*.-pinacolyl alcohol and the alcohol obtained from pinacolin appear therefore to be distinct substances possessing different physical properties, but yielding the same derivatives (chloride, bromide, acetate). The formation of the same derivatives from the two alcohols is similar to the transformation of the group

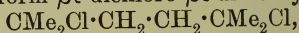


into  $\text{CMe}_2\cdot\text{CMe}_2$  by the action of hydrogen bromide on  $\gamma\gamma$ -dimethyl- $\Delta^{\alpha}$ -butylene (this vol., i, 477).  
T. A. H.

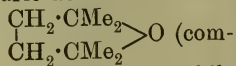
### Succinic Pinacone [ $\beta\epsilon$ -Dimethylhexane- $\beta\epsilon$ -diol],



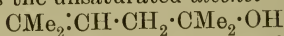
LOUIS HENRY (*Compt. rend.*, 1906, 143, 496—500).— $\beta\epsilon$ -Dimethylhexane- $\beta\epsilon$ -diol (compare Zelinsky, *Abstr.*, 1902, i, 593; and Valeur, *Bull. Soc. chim.*, 1902, 27, 1139), readily obtained by the action of magnesium methyl bromide on ethyl lævulate, behaves like a tertiary alcohol (this vol., i, 133, 329), and reacts with fuming hydrochloric acid or acetyl chloride to form  $\beta\epsilon$ -dichloro- $\beta\epsilon$ -dimethylhexane,



which crystallises in plates or needles melting at 66—67°, boils and decomposes at 180°, and is identical with the compound obtained by the action of hydrochloric acid on diisocrotonyl or diisobutenyl (Pogorželsky, *Abstr.*, 1899, i, 785).  $\beta\epsilon$ -Dimethylhexane- $\beta\epsilon$ -diol is readily dehydrated by the action of dilute sulphuric acid even in the cold to form *s*-tetramethyltetramethylene oxide,



(compare Pogorželsky, *Abstr.*, 1899, i, 785), which is a colourless, mobile liquid with an agreeable odour, boils at 116—117°, and reacts even in the cold with fuming hydrochloric acid to form  $\beta\epsilon$ -dichloro- $\beta\epsilon$ -dimethylhexane. When  $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol is distilled, it suffers partial dehydration and forms the unsaturated alcohol



[ $\beta\epsilon$ -dimethyl- $\Delta^{\epsilon}$ -hexylene- $\beta$ -ol], which is a colourless, mobile liquid with an agreeable penetrating odour, boils at 165°, combines readily with bromine, and is converted into its chloride by the action of acetyl chloride.  
M. A. W.

Distillation of Ether. E. J. SWAAB (*Chem. Centr.*, 1906, ii, 841; from *Pharm. Weekblad*, 1906, 43, 817—818).—A glass attachment is described, enabling a reflux condenser to be used, the condensed ether passing down a vertical tube into the receiver, the vapour entering by means of a side branch.  
P. H.

Freezing and Melting Points of Glyceryl Nitrate. HERMANN KAST (*Chem. Centr.*, 1906, ii, 948; from *Zeit. ges. Schiess, Sprengstoffwesen*, 1, 225—228).—Glyceryl nitrate exists in two modifications. The labile form melts at 2·8—2·9° and solidifies at 2·0—2·2°, whilst the stable form melts at 13·1—13·2° and solidifies at 12·5°. The labile



form has a more glassy appearance than the other. It is very difficult to freeze small quantities, but less so to freeze large quantities, of glyceryl nitrate; in a mixture of ether and carbon dioxide it solidifies to an amorphous mass which, however, becomes liquid on warming to temperatures below the true freezing point; when once it has been frozen it is less difficult to freeze it a second time. The depression of the freezing point of glyceryl nitrate by dinitrochlorohydrin agrees fairly closely with Raoult's law.

P. H.

**Origin of Optically Active Fatty Acids in Nature.** CARL NEUBERG (*Chem. Centr.*, 1906, ii, 1132—1133; from *Biochem. Zeit.*, 1906, 1, 368—379).—The author has obtained experimental evidence in support of his theory that mineral oil originates from the optically active decomposition products of proteids. The fatty acids isolated from a sample of putrid cheese yielded a fraction comprising from acetic to hexoic acid which had  $\alpha_D + 1.2^\circ$ . The volatile acids obtained from putrid gelatin were similarly active, but to a less degree. Further, by the action of lipase from vegetable sources on the triglyceride of dibromostearic acid, free dextrorotatory dibromostearic acid and a dextrorotatory glyceride were obtained, showing that as a result of slow oxidation and asymmetric fission by living or unorganised ferments, inactive fats may give rise to optically active substances.

P. H.

**Active Components of  $\alpha$ -Bromopropionic Acid.** LUDWIG RAMBERG (*Annalen*, 1906, 349, 324—332. Compare Abstr., 1901, i, 63; Warburg and Fischer, Abstr., 1905, i, 692).—The resolution of the inactive acid can be effected without great loss of material by a method involving fractional crystallisation of the cinchonine salt and "freezing" out the inactive acid from the active acids so obtained. A supersaturated solution of the salt,  $C_{19}H_{23}ON_2 \cdot 2C_3H_5O_2Br$ , is made by dissolving 153 grams of the acid and 148 grams of cinchonine in 3 litres of water at  $30-35^\circ$ , the last 25 per cent. of the acid being added slowly after the base has dissolved. After evaporating the solution at  $27-30^\circ$  in a vacuum to 2,300 c.c., the crystals (fraction I.) are removed and the mother liquor evaporated to about 1,400 c.c. and the second crop of crystals (fraction II.) filtered off. The solution of these crystals is employed in dissolving a fresh quantity of cinchonine and of the racemic acid. The acid from fraction I. ( $\alpha_D - 11^\circ$ ) and that from the mother liquor from fraction II. ( $\alpha_D + 19^\circ$ ) are treated separately as follows. The temperature is raised to the highest at which crystallisation will begin, the acid is nucleated with a crystal of the racemic form, and the temperature allowed to fall very slowly for several days. When half the acid has solidified, the crystals are separated centrifugally, and consist of the pure racemic form. The liquid is again nucleated and cooled slowly to  $0^\circ$ , whereby a further quantity of the racemic form is obtained. The acid which still remains liquid has  $\alpha_D \pm 33^\circ$ , and after a third nucleation at  $-5^\circ$ , cooling to  $-15^\circ$ , and removal of the crystals, has  $\alpha_D \pm 38^\circ$ . The cinchonine salt of this acid is recrystallised six or eight times from water or acetone. The recovered *l*- $\alpha$ -bromopropionic acid solidifies completely at  $-40^\circ$ ;

when the temperature is raised slowly to  $-7^{\circ}$  and then lowered to  $-12^{\circ}$ , the crystals obtained, after removal of the liquid portion, consist of the pure lævo-acid. It melts at  $-6^{\circ}$  to  $-7^{\circ}$ , has a sp. gr. 1.708 at  $20^{\circ}/20^{\circ}$ , and  $[\alpha]_D -27^{\circ}$  at  $20^{\circ}$  (compare Warburg, *loc. cit.*). The pure *d*-acid has not been obtained; the *ethyl* ester of an acid having  $\alpha_D +36.33^{\circ}$  boils at  $62-63^{\circ}$  under 15 mm. pressure, has a sp. gr. 1.388 at  $20^{\circ}/4^{\circ}$ , and  $\alpha_D +36.35^{\circ}$  at  $20^{\circ}$ . The pure ester should have  $\alpha_D +46^{\circ}$  and  $[\alpha]_D +33^{\circ}$  at  $20^{\circ}$  (compare Walker, *Trans.*, 1895, 67, 921). C. S.

**Theory of Saponification.** JULIUS MARCUSSE (Ber., 1906, 39, 3466—3474).—According to Lewkowitsch (*Proc.*, 1899, 15, 190) incompletely hydrolysed fats should contain mono- and di-glycerides, and the presence of these substances should be indicated by a high acetyl value; but as other compounds, such as hydroxy-acids, lactones, &c., are also indicated by the acetyl value, the author has endeavoured to isolate the lower glycerides and thus obtain further support for the theory of successive hydrolysis.

A quantity of incompletely saponified fat was divided into two equal parts. One was acidified, and the precipitated neutral fat and free fatty acid acetylated directly; from the other portion, after removing excess of alkali with acid, the soaps were extracted and the residual neutral fat acetylated. Finally, the fatty acids from the soaps of the second portion were acetylated. The anticipated increase in the acetyl value was never observed. The portion containing both neutral fat and free fatty acid usually gave a slightly higher acetyl value than that of the neutral fat, and the acetyl value of the separated acids were sometimes as high as, and sometimes higher than, that of the neutral fat. These results do not point to the existence of the lower glycerides, but seem to depend on certain changes which have occurred in the fatty acids.

The saponification of olive oil by shaking with concentrated aqueous sodium hydroxide in stoppered vessels excludes the interference of atmospheric oxygen and affords scope for the hydrolysis to occur in successive stages, but no indication of the formation of the lower glycerides was obtained. Saponification of this oil in the cold with the enzyme of castor oil seeds gave no indication of successive hydrolysis. The hydrolytic changes which occur in rancid fats do not give rise to the lower glycerides, for although diercein is found in old rape-seed oil, yet it only occurs in the oil which has been refined with sulphuric acid, and in all probability arises as a fission product of triercein, formed, not by alkaline hydrolysis, but by the action of the acid. The examination of rancid sheep's tallow and olive oil gave no indubitable evidence of the presence of mono- and di-glycerides.

G. T. M.

**Beeswax from Annam.** J. BELLIER (*Ann. Chim. anal.*, 1906, 11, 366—368).—A sample of yellow beeswax received from Annam gave results, on analysis, which differed considerably from those yielded by ordinary European beeswax. The figures obtained were: sp. gr. 0.964; m. p.  $61^{\circ}$ ; acid number, 7.8; ester number, 86.6; iodine number, 6; unsaponifiable matter, 10.5 per cent. W. P. S.

**Historical Note on the Fixation of Ozone by Oleic Acid.** THEODOR WEYL (*Ber.*, 1906, 39, 3347—3348).—The author claims to have been the first to observe the fixation of ozone by acids of the oleic series (compare Molinari, this vol., i, 792; Harries, *ibid.*, i, 793).  
E. F. A.

**Separation of the Fatty Acids of Cod-liver Oil.** HENDRIK BULL (*Ber.*, 1906, 39, 3570—3576. Compare Abstr., 1900, ii, 250, 325; 1901, ii, 137; Ljubarsky, Abstr., 1898, ii, 299).—The fatty acids of cod-liver oil are separated by conversion into the methyl esters, fractional distillation of these under 10 mm. pressure, when 80 per cent. of the esters distil below 240°, and hydrolysis of the fractions so obtained. In this manner have been isolated myristic, palmitic, stearic, oleic, and erucic acids, as also two new acids,  $C_{16}H_{30}O_2$ , and  $C_{20}H_{38}O_2$ .

The unsaturated acid  $C_{16}H_{30}O_2$ , which is present to the extent of 6 per cent. of the cod-liver oil, and is obtained also from herring and whale oils, melts at  $-1^\circ$ , has an acid number 219, and an iodine number 91.5, forms a *methyl* ester boiling at 185—186° under 10 mm. pressure, and on oxidation with potassium permanganate in alkaline solution cooled with ice, yields a *dihydroxypalmitic acid* crystallising in white leaflets and melting at 125°. The *acetyl* derivative of this acid has an acetyl number 355.7.

*Gadoleic acid*,  $C_{20}H_{38}O_2$ , obtained together with stearic and oleic acids on hydrolysis of the fraction boiling at 205—206° under 10 mm. pressure, occurs also in herring and whale oils; it melts at 24.5°, and has an acid number 180.5, and an iodine number 80.3. On oxidation with potassium permanganate in alkaline solution cooled with ice, it yields *dihydroxygadoleic acid*,  $C_{20}H_{38}O_2(OH)_2$ , which separates from alcohol in white crystals, melts at 127.5—128°, and has an acid number 161.7.

Heyerdahl's jecoleic acid (*Cod-liver Oil and its Chemistry*), if present, can be so only in very small amount, whilst this author's dihydroxy-acid is probably a eutectic compound of oleic and gadoleic acids.

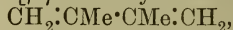
G. Y.

**Action of Alkali Carbonates on  $\beta\gamma$ -Dibromo- $\alpha\alpha$ -dimethyl Acids.** Part II. ALFRED COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 969—988. Compare this vol., i, 788).— $\beta\gamma$ -Dibromo- $\alpha\alpha\beta$ -trimethylbutyric acid, on treatment with zinc dust, furnishes dimethylisopropenylacetic [ $\alpha\alpha$ -dimethyl- $\beta$ -methylenebutyric] acid, and reacts with a dilute solution of potassium hydrogen carbonate, forming dimethylisopropenylcarbinol. With potassium carbonate the action proceeds further, and in addition to the alcohol some pinacolin and diisopropenyl are formed. The latter is the principal product obtained when  $\beta\gamma$ -dibromo- $\alpha\alpha\beta$ -trimethylbutyric acid is treated with pyridine in presence of ether.

Dimethylisopropenylcarbinol,  $CH_2 \cdot CMe \cdot CMe_2 \cdot OH$ , is a mobile liquid of pleasant odour, melts at  $-17^\circ$  (compare Choupotsky and Mariutza, Abstr., 1890, 727). The *phenylcarbamate* separates from boiling light petroleum in long needles and melts at 103—104°. On dehydration



with sulphuric acid, the alcohol yields a mixture of diisopropenyl and pinacolin. Diisopropenyl [ $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene],



has a sp. gr. 0.73074 at  $15^\circ$ ,  $n_a$  1.4379,  $n_\beta$  1.4527,  $n_\gamma$  1.4622, and  $n_D$  1.4421, and on oxidation with permanganate yields acetic and formic acids and a small quantity of pinacolin. The dibromide,  $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CMe}:\text{CH}_2$ , melts at  $49^\circ$ , boils at  $105^\circ$  under 14 mm. pressure, and regenerates the hydrocarbon on treatment with magnesium in presence of ether (compare Kondakoff, Abstr., 1901, i, 62). The tetrabromide melts at  $140^\circ$  [compare (1) Mariutza and (2) Kondakoff (*loc. cit.*)]. The oily bromide referred to by Kondakoff (*loc. cit.*) boils at  $115^\circ$  under 14 mm. pressure, and is probably a mixture of the dibromide with other more highly brominated derivatives.

Dimethylallylcarbinol,  $\text{CH}_2:\text{CH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ , obtained by condensing acetone with allyl iodide in presence of zinc, is a mobile liquid and boils at  $120^\circ$  under atmospheric pressure (compare Saytzeff, Abstr., 1877, ii, 298). The *phenylcarbamate* crystallises from boiling light petroleum in slender needles and melts at  $49$ – $50^\circ$ .

When ethyl methylacrylate reacts with magnesium methyl iodide, dimethylisopropenylcarbinol, diisopropenyl, and  $\alpha\alpha$ -methylethylacetone [*methyl  $\alpha$ -methylpropyl ketone*] are produced (compare Kohler, Abstr., 1904, i, 595).  $\alpha\alpha$ -Methylethylacetone may also be prepared by treating ethyl acetoacetate with ethyl and methyl iodides successively in presence of sodium and alcohol and hydrolysing the complex ester so formed. The ketone is liquid, has a penetrating camphoraceous odour, and boils at  $116^\circ$  under atmospheric pressure; the *semicarbazone* crystallises from ether and melts at  $95$ – $96^\circ$ ; the *oxime* is a pungent smelling liquid and boils at  $89^\circ$  under 20 mm. pressure; the *phenylhydrazone* is viscid and boils at  $152^\circ$  under 10 mm. pressure.

Diethylisopropenylcarbinol,  $\text{CH}_2:\text{CMe}:\text{CET}_2\cdot\text{OH}$ , the sole product of the action of magnesium ethyl iodide on ethyl methylacrylate, is a mobile liquid with a camphoraceous odour and boils at  $152^\circ$ .

Methylpropenylcarbinol,  $\text{CHMe}:\text{CHMe}\cdot\text{CH}\cdot\text{OH}$ , the sole product of the action of magnesium methyl iodide on crotonaldehyde, boils at  $122^\circ$  under atmospheric pressure (compare Grignard, Abstr., 1901, i, 679); the *acetate* boils at  $138^\circ$ , and the *phenylcarbamate* crystallises from light petroleum and melts at  $43^\circ$ .

By the action of magnesium methyl iodide on ethyl  $\beta\beta$ -dimethylacrylate, dimethylpentadiene, dimethylisobutenylcarbinol, and a *ketone* yielding a *semicarbazone* crystallising in long needles and melting at  $123$ – $124^\circ$  are obtained. This ketone may be  $\psi$ -butylacetone,  $\text{CMe}_3\cdot\text{CH}_2\cdot\text{CMe}$ . Attempts to synthesise  $\psi$ -butylacetone by condensing *tert.*-butyl chloride with trioxymethylene in presence of magnesium yielded only Tissier's alcohol,  $\text{CMe}_3\cdot\text{CH}_2\cdot\text{OH}$ . The *iodide* prepared from the latter, by condensation with acetyl chloride in presence of zinc, yielded only traces of the ketone sought, and similarly attempts to prepare the ketone from ethylacetoacetate were unsuccessful.

Dimethylisobutenylcarbinol,  $\text{CMe}_2:\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$ , is the principal product of the interaction of magnesium methyl iodide and ethyl methylacrylate. It has a camphoraceous odour and boils at  $138^\circ$  under atmospheric pressure (compare von Fellenberg, Abstr., 1904,

i, 961). The *phenylcarbamate* crystallises in silky needles and melts at  $111^{\circ}$ .  $\beta\delta$ -Dimethyl- $\Delta^{\gamma}$ -pentadiene,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$ , also produced in the above reaction (compare Grignard, Abstr., 1900, i, 382), boils at  $90^{\circ}$  under atmospheric pressure; the *dibromide* has an irritating odour and boils at  $65^{\circ}$  under 10 mm. pressure.

The foregoing results show that the fixation of magnesium alkyl haloids by the  $\alpha\beta$ -unsaturated esters of the aliphatic series is confined to magnesium methyl iodide, and in this respect differ from those obtained by Kohler (Abstr., 1904, i, 595) and by Kohler and Heritage (Abstr., 1905, i, 207) with unsaturated compounds of the cyclic series.

When  $\beta\gamma$ -dibromo- $\beta$ -phenyl- $\alpha\alpha$ -dimethylbutyric acid is treated with an aqueous solution of potassium carbonate,  $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha\alpha$ -dimethylbutyrolactone,  $\begin{array}{c} \text{CPh(OH)}\cdot\text{CMe}_2 \\ | \\ \text{CH}_2\text{---O} \end{array} > \text{CO}$ , and *phenylisoprene* are produced.

The former crystallises from a mixture of ether and light petroleum and melts at  $115^{\circ}$ . Phenylisoprene is a mobile odorous liquid, boils at  $95^{\circ}$  under 24 mm. pressure and yields a liquid dibromide. When dissolved in carbon disulphide and treated with bromine, it furnishes a crystalline *product* which may be a monobromo-derivative of the dibromide; it melts at  $76^{\circ}$ . T. A. H.

$\gamma$ -Aldehydo-acids. EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], 35, 989—1004. Compare Abstr., 1905, i, 562).—When  $\beta\gamma$ -dibromo- $\alpha\alpha$ -dimethylbutyric acid is distilled, it decomposes, yielding  $\gamma$ -bromo- $\alpha\alpha$ -dimethylbutyrolactone (this vol., i, 788), and this, when boiled with quinoline, furnishes isoprene. Ethyl  $\beta\gamma$ -dibromo- $\alpha\alpha$ -dimethylbutyrate, obtained by the action of bromine on ethyl dimethylvinylacetate, is readily hydrolysed either by potassium hydroxide or acetate dissolved in water, and therefore yields the same products as the free acid when treated with these reagents.

$\beta$ -Bromo- $\alpha\alpha$ -dimethylvalerolactone, when heated in presence of quinoline, yields the corresponding unsaturated lactone,  $\begin{array}{c} \text{CH}\cdot\text{CMe}_2 \\ | \\ \text{CMe---O} \end{array} > \text{CO}$ , and this, when dissolved in an aqueous solution of potassium hydroxide, yields mesitonic acid,  $\text{CH}_2\text{Ac}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ .

$\beta\gamma$ -Dibromo- $\alpha\alpha\beta$ -trimethylbutyric acid (Abstr., 1905, i, 562) crystallises from light petroleum and melts at  $107$ — $108^{\circ}$ . When heated, it furnishes first the corresponding bromolactone,  $\begin{array}{c} \text{CMeBr}\cdot\text{CMe}_2 \\ | \\ \text{CH}_2\text{---O} \end{array} > \text{CO}$ , which crystallises in parallelopipeds and melts at  $194^{\circ}$ , and finally the unsaturated lactone,  $\begin{array}{c} \text{CMe}\cdot\text{CMe}_2 \\ | \\ \text{CH---O} \end{array} > \text{CO}$ , which is crystalline at low temperatures, melts at  $-25^{\circ}$ , boils at  $65^{\circ}$  under 12 mm. or at  $174^{\circ}$  under atmospheric pressure, and on hydrolysis (*loc. cit.*) furnishes  $\gamma$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyrolactone,  $\begin{array}{c} \text{CMe}_2\text{---CO} \\ | \\ \text{OH}\cdot\text{CH}\cdot\text{CHMe} \end{array} > \text{O}$ . The *ethyl ether* of this is a mobile liquid and boils at  $107^{\circ}$  under 11 mm. pressure; the acetate (*loc. cit.*) boils at  $135^{\circ}$  under 11 mm. pressure. On treatment with semicarbazide hydrochloride in presence of sodium

acetate, the hydroxylactone yields *trimethylsuccinic hemialdehyde semicarbazone*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CH} \cdot \text{CHMe} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , which forms small crystals and melts and decomposes at  $240^\circ$ . The corresponding *oxime*, obtained in an analogous manner, melts and decomposes at  $153^\circ$ , and the *phenylhydrazone* melts at  $110^\circ$ .

On oxidation with chromic acid,  $\gamma$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyrolactone yields trimethylsuccinic acid.

$\beta\gamma$ -Dibromo- $\alpha\alpha\beta$ -trimethylbutyrolactone, obtained by the action of bromine on the unsaturated bromolactone mentioned previously, melts at  $107$ — $108^\circ$ .

$\gamma$ -Bromo- $\alpha\alpha$ -dimethylisopropenylacetic acid,  $\text{CHBr} \cdot \text{CMe} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , obtained by heating methyl  $\beta\gamma$ -dibromo- $\alpha\alpha\beta$ -trimethylbutyrate with potassium hydroxide dissolved in water, crystallises from light petroleum and melts at  $59^\circ$ . Its *methyl ester*, prepared from  $\beta\gamma$ -dibromo- $\alpha\alpha\beta$ -trimethylbutyrate, is a mobile liquid and boils at  $104^\circ$  under 19 mm. pressure.

$\beta$ -Bromo- $\beta$ -phenyl- $\alpha\alpha$ -dimethylbutyrolactone, obtained by heating  $\beta\gamma$ -dibromo- $\beta$ -phenyl- $\alpha\alpha$ -dimethylbutyric acid at  $220^\circ$  under 30 mm. pressure, crystallises from a mixture of ether and light petroleum in brilliant lamellæ, melts at  $131^\circ$ , and, when boiled with quinoline, yields *phenyldimethylbutenolide*,  $\begin{array}{c} \text{CPh} \cdot \text{CMe}_2 \\ || \\ \text{CH} \text{---} \text{O} \end{array} > \text{CO}$ , which crystallises from ether, melts at  $70$ — $71^\circ$ , boils at  $145^\circ$  under 10 mm. pressure, and on hydrolysis yields  $\gamma$ -hydroxy- $\beta$ -phenyl- $\alpha\alpha$ -dimethylbutyrolactone. This forms brilliant spangles from benzene, begins to decompose at  $120^\circ$ , melts at  $131^\circ$ , and, with semicarbazide hydrochloride in presence of sodium acetate, yields *phenyldimethylsuccinic hemialdehyde semicarbazone*, which crystallises from alcohol and melts and decomposes at  $220^\circ$ . The corresponding *oxime* is crystalline, begins to decompose at  $140^\circ$ , and melts at  $155^\circ$ . The *hydroxylamine* salt of the oxime melts and decomposes at  $130^\circ$ . By the action of hydrazine hydrate on the  $\gamma$ -hydroxy-lactone (2 mols.), *phenyldimethylsuccinic hemialdehydeazine*,  $\text{N}_2(\text{:CH} \cdot \text{CHPh} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H})_2$ , is produced; it crystallises from alcohol and melts at  $210^\circ$ .

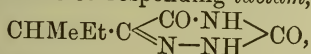
$\beta$ -Phenyl- $\alpha\alpha$ -dimethylsuccinic acid, obtained by oxidising the hydroxylactone with chromic acid, separates from ether in small crystals and melts and decomposes at  $180^\circ$ .

T. A. H.

**Preparation of Methyleneethylpyruvic Acid and its Derivatives.** RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 962—965).—Most of the facts recorded in this paper are already given in Abstr., 1905, i, 636. Ethyl *sec*.-butylacetoacetate, prepared by the general method (Abstr., 1904, i, 646), yields with hydrazine hydrate, 3-methyl-4-*sec*.-butyl-5-pyrazolone, which crystallises from boiling benzene and melts at  $158$ — $159^\circ$ . When ethyl *sec*.-butylacetoacetate is treated with nitrosylsulphuric acid (Bouveault and Locquin, Abstr., 1904, i, 847), it furnishes ethyl  $\alpha$ -oximino- $\beta$ -methylvalerate (Abstr., 1905, i, 636), a thick liquid which has a sp. gr. 1.042 at  $0^\circ/4^\circ$ . This is hydrolysed by potassium hydroxide in water and furnishes the corresponding acid (*loc. cit.*), which separates from ether in brilliant spangles and melts, sublimes, and decomposes at  $160$ — $161^\circ$ . Further, the ethyl methyl-



ethylpyruvate, formed by treating the oximino-ester with freshly-formed nitrous acid (Bouveault and Locquin, *Abstr.*, 1905, i, 10), is a colourless liquid which has a sp. gr. 0.988, boils at 78—79° under 15 mm. pressure, and is hydrolysed less easily than its analogues. The semicarbazone separates, on cooling its solution in light petroleum, in slender needles, melts at 82—83°, and, on treatment with potassium hydroxide solution at 100°, furnishes, not the semicarbazone of methyl-ethylpyruvic acid, but the corresponding *lactam*,



which crystallises from benzene on addition of alcohol in spangles and melts at 206—207°.

Ethyl methylethylpyruvate, when heated with water in a closed tube for several hours, furnishes the acid which boils at 84° under 15 mm. pressure (?), melts at 35°, furnishes a phenylhydrazone melting at 130° and a semicarbazone which crystallises from dilute alcohol and melts at 165°.

T. A. H.

[*β*-Ethoxymethylacrylic Acid]. OSKAR EMMERLING and L. KRISTELLER (*Ber.*, 1906, 39, 3549—3550).—*β*-Ethoxymethylacrylic acid, recently described by the authors (this vol., i, 623), is the same substance as that prepared lately by Tschitschibabin (this vol., i, 398).

G. T. M.

**Isomorphism.** JEAN HERBETTE (*Chem. Centr.*, 1906, ii, 970; from *Bull. Soc. franç. Min.*, 29, 97—190).—By special methods of crystallisation the following new crystalline forms of previously known compounds have been obtained. (1) A rhombohedral form of thallium tartrate,  $\text{C}_4\text{H}_4\text{O}_6\text{Ti}_2$  [ $a:c = 1:1.08534$ ], sp. gr. 4.8; (2) a rhombic hydrated thallium tartrate,  $2\text{C}_4\text{H}_4\text{O}_6\text{Ti}_2 \cdot \text{H}_2\text{O}$ ; these salts are completely isomorphous with the rubidium and potassium salts respectively; (3) a substance obtained by crystallising a mixture of barium chloride and bromide. For details of these compounds the original paper should be consulted.

P. H.

**Action of Formaldehyde Solution on Potassium Permanganate.** GEORGE B. FRANKFORTER and RODNEY M. WEST (*J. Amer. Chem. Soc.*, 1906, 28, 1234—1238).—A study on the action of formalin on solid potassium permanganate. In order to avoid a too violent action, the powdered permanganate should be diluted with an equal bulk of sand. In order to obtain the largest possible amount of gaseous formaldehyde (which may then be absorbed in water and titrated), 50 c.c. of strong formalin should be dropped slowly (so as to take about thirty minutes) on to 200 grams of the permanganate-sand mixture. A special apparatus is described and illustrated, and two tables are given.

L. DE K.

**Action of Bases on Chloral Hydrate.** JOHANNES E. ENKLAAR (*Rec. trav. chim.*, 1906, 25, 297—310).—The author has extended his investigation on the rate of decomposition of chloral hydrate by the action of bases (*Abstr.*, 1905, i, 171, 741), and in the present paper the values of the velocity coefficient are tabulated for mixtures of chloral hydrate and barium hydroxide, with and without the addition of neutral barium nitrate, chloride, acetate, propionate, or valerate. The

results show that, as in the case of the other alkali or alkali-earth hydroxides, the velocity of the reaction increases with the excess of the free base above the equivalent of the chloral hydrate employed, and is accelerated by the addition of neutral salts, equivalent quantities of different salts producing the same effect. M. A. W.

**Succinaldehyde Derivatives.** CARL D. HARRIES and HERMANN KRÜTZFELD (*Ber.*, 1906, 39, 3670—3677. Compare Abstr., 1901, i, 451; 1902, i, 345; this vol., i, 227; Wohl and Schweitzer, *ibid.*, i, 232).—In the preparation of succindialdehyde from its dioxime by means of nitrous gases, it is advisable to pass the gases for some time after all the oxime has dissolved, as otherwise, after neutralising with calcium carbonate and evaporating, an explosive syrup is obtained. If the gas is passed for too long a time a precipitate of succinic acid appears.

*Succinaldehydedisemicarbazone*,  $C_6H_{12}O_2N_6 \cdot H_2O$ , crystallises from water, in which it is readily soluble, in the form of six-sided prisms, melting at  $188^\circ$ . It dissolves readily in methyl, less readily in ethyl alcohol. The diphenylmethylhydrazone melts at  $96^\circ$ , and not at  $86^\circ$  (Henle, Abstr., 1905, i, 413).

The *di-nitrophenylhydrazone*  $C_{16}H_{16}O_4N_6 \cdot H_2O$ , crystallises in golden yellow needles melting at  $185^\circ$  and is insoluble in water.

The product  $C_{10}H_{10}N_2 \cdot H_2O$ , obtained by the condensation of succinaldehyde with *o*-phenylenediamine, is a yellow, amorphous powder with feebly basic properties. It melts at about  $150^\circ$ , but after heating at  $100^\circ$  is anhydrous and then melts at about  $177^\circ$ . It dissolves in benzene or chloroform, but is insoluble in water, alcohol or light petroleum.

Succintetramethylacetal is readily converted into its *dibromo-derivative*,  $CH(OMe)_2 \cdot CHBr \cdot CHBr \cdot CH(OMe)_2$ , when treated with an excess of bromine in the presence of calcium carbonate in sunlight. It is a colourless oil readily soluble in organic solvents, and when heated evolves hydrogen bromide.

*Dibromosuccinaldehyde*, obtained by brominating the aldehyde in chloroform solution in the presence of calcium carbonate, is a yellow oil with a strong odour. It readily reduces Fehling's solution, but does not give the pyrrole reaction. When dissolved in warm acetic acid and precipitated with water, it is converted into a solid modification melting at  $75^\circ$  after sintering at about  $50^\circ$ .

When distilled under reduced pressure, the dibromo-derivative is converted into *bromofumaraldehyde*, which distils at  $130^\circ$  under 15 mm. pressure. The *tetra-acetal* distils at  $110$ — $120^\circ$  under 15 mm. pressure. J. J. S.

**Thio-derivatives of Ketones.** III. EMIL FROMM and PAUL ZIERSCH (*Ber.*, 1906, 39, 3599—3609. Compare Baumann and Fromm, Abstr., 1890, 26; 1895, i, 362; Fromm and Mangler, Abstr., 1901, i, 184).—1 : 3-Diketones react with hydrogen sulphide in presence of hydrogen chloride, forming thio-derivatives of the bisdiketones.

*Tetrathiobisacetylacetone*,  $S \begin{array}{c} \diagup \\ \text{CMe} \cdot \text{CH}_2 \cdot \text{CMe} \\ > S \\ \diagdown \\ \text{CMe} \cdot \text{CH}_2 \cdot \text{CMe} \end{array} S$ , separates from

boiling alcohol in white crystals, melts at  $161^{\circ}$ , remains unchanged when boiled with alcoholic potassium hydroxide, or when distilled alone or with zinc dust or copper powder, dissolves in concentrated sulphuric acid and is reprecipitated on dilution, and reacts with bromine in chloroform solution, evolving hydrogen bromide and forming an unstable crystalline substance. When heated with methyl iodide at  $100^{\circ}$ , it yields trimethylsulphine iodide.

With hydrogen sulphide methylacetylacetone yields two products:

*trithio-oxybismethylacetylacetone*,  $\text{S} \begin{array}{c} \text{CMe} \cdot \text{CHMe} \cdot \text{CMe} \\ > \text{S} \\ \text{CMe} \cdot \text{CHMe} \cdot \text{CMe} \end{array} \text{S} \begin{array}{c} \text{CMe} \cdot \text{CHMe} \cdot \text{CMe} \\ > \text{S} \\ \text{CMe} \cdot \text{CHMe} \cdot \text{CMe} \end{array} \text{O}$ , which melts

at  $100^{\circ}$ , is readily soluble in chloroform or alcohol, and is obtained only in a slightly impure condition, and *trithiobismethylacetylacetone*,

$\text{S} \begin{array}{c} \text{CMe} \cdot \text{CHMe} \cdot \text{C}(\text{CH}_2) \\ > \text{S} \\ \text{CMe} \cdot \text{CHMe} \cdot \text{C}(\text{CH}_2) \end{array} \text{S}$ , or  $\text{S} \begin{array}{c} \text{CMe} \cdot \text{CMe} \cdot \text{CMe} \\ > \text{S} \\ \text{CMe} \cdot \text{CMe} \cdot \text{CMe} \end{array} \text{S}$ , which is pre-

cipitated on addition of alcohol to its solution in chloroform and melts at  $193^{\circ}$ .

*Tetrathiobisdimethylacetylacetone*,  $\text{S} \begin{array}{c} \text{CMe} \cdot \text{CMe}_2 \cdot \text{CMe} \\ > \text{S} \\ \text{CMe} \cdot \text{CMe}_2 \cdot \text{CMe} \end{array} \text{S}$ , melts at

$227^{\circ}$ , and is soluble in chloroform, but insoluble in alcohol.

These thio-derivatives of the 1:3-diketones are oxidised by shaking the benzene solution with concentrated aqueous potassium permanganate and dilute sulphuric acid.

Tetrathiobisacetylacetone yields two oxidation products: *trithio-tetraoxybisacetylacetone*,  $\text{C}_8\text{H}_{14}\text{O}_4\text{S}_3$ , melts at  $275^{\circ}$ , is soluble in hot water, but is almost insoluble in cold water or alcohol, and is decomposed by aqueous alkali hydroxides. *Trithiotrioxobisacetylacetone*,  $\text{C}_8\text{H}_{14}\text{O}_3\text{S}_3$ , crystallises from water in which it is more soluble than the tetrathiotetraoxy-compound, and melts at  $225^{\circ}$ . On further oxidation, the two preceding substances yield *trithiopentaoxybisacetylacetone*,  $\text{C}_8\text{H}_{14}\text{O}_5\text{S}_3$ , which crystallises from water and melts at  $293^{\circ}$ .

*Trithiotrioxobismethylacetylacetone*,  $\text{C}_{10}\text{H}_{16}\text{O}_3\text{S}_3$ , formed by oxidation of trithiobismethylacetylacetone, separates from alcohol in white crystals and melts at  $255^{\circ}$ .

*Tetrathiotetraoxybisdimethylacetylacetone*,  $\text{C}_{14}\text{H}_{24}\text{O}_4\text{S}_4$ , forms glistening, white crystals and decomposes at about  $350^{\circ}$ . G. Y.

**Fermentation of Sugar without Enzymes.** H. SCHADE (*Zeit. physikal. Chem.*, 1906, 57, 1—46).—When an alkaline solution of dextrose is kept at a temperature rather above the ordinary, slow decomposition takes place, and the solution assumes a yellow or brown colour. If hydrogen peroxide has been added to the solution in sufficient quantity, no coloration is observed, even after the lapse of weeks; should there cease to be excess of hydrogen peroxide, the brown colour appears, but it can be destroyed if a little of the peroxide is added immediately after its appearance. It is shown that the brown colour is due to the action of alkali on acetaldehyde, which is produced in the decomposition of the sugar, and the preventive effect of the hydrogen peroxide consists in removing the acetaldehyde



by oxidation to acetic acid. This view is in harmony also with experiments by Framm (Abstr., 1897, i, 5), and others by the author, which show that the production of the brown colour may be prevented also by (1) working under diminished pressure, and so removing the volatile aldehyde, (2) passing a rapid current of oxygen, hydrogen, or nitrogen through the solution, or (3) adding ammonia, sodium hydrogen sulphite, or potassium cyanide—substances which fix the aldehyde.

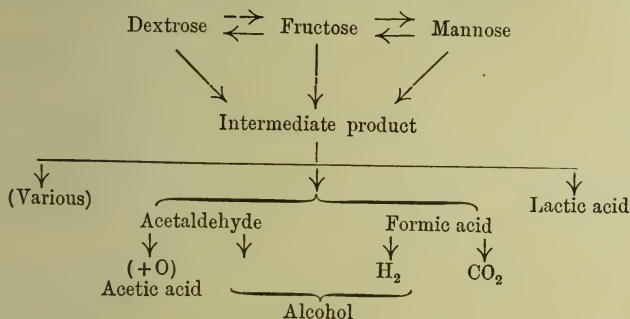
When such means are used to prevent the formation of a brown colour, the two products of the slow decomposition of the sugar (dextrose or lævulose) under the influence of alkali are formic acid and acetaldehyde. Other substances, for example, lactic acid, may be produced, but to an extent which is negligible so far as the main character of the decomposition is concerned.

For every molecule of sugar decomposed, two molecules of formic acid are produced, and it has further been shown, in a less direct manner, that for every molecule of sugar decomposed two molecules of acetaldehyde are produced. Thus the decomposition may be represented by the equation  $C_6H_{12}O_6 = 2CH_3 \cdot CHO + 2H \cdot CO_2H$ . Galactose and mannose, although but few experiments have been made with them, appear to undergo a similar decomposition. The substances which were found to promote the sugar decomposition in question were potassium and sodium hydroxides, potassium, sodium and lithium carbonates, and disodium hydrogen phosphate. The decomposition is thus a catalysis by the  $OH'$  ion, and the velocity of decomposition is proportional to the concentration of that ion.

When a solution of sodium formate, slightly acidified with acetic acid and containing some finely-divided rhodium ("rhodium black") in suspension, is warmed under a reflux condenser, decomposition into carbon dioxide and hydrogen readily takes place. If, however, an amount of acetaldehyde equivalent to the sodium formate is distilled into the sodium formate solution while the latter is being heated, a yield of 60—70 per cent. of ethyl alcohol is obtained. That is, acetaldehyde and formic acid have reacted under the influence of a catalytic agent to form ethyl alcohol and carbon dioxide. Hence ethyl alcohol and carbon dioxide may be obtained from sugars by a purely chemical decomposition, and the change involved in fermentation may be realised without the intervention of enzymes.

The equation  $C_6H_{12}O_6 = 2CH_3 \cdot CHO + 2H \cdot CO_2H$  must not be regarded as excluding the possible formation of intermediate products, and in fact it is extremely probable that such are formed. Lactic acid is especially referred to in this connexion, and it is pointed out that, although only traces of this acid were found in the author's experiments, yet when the alkali concentration is high and the solutions are brown in colour considerable quantities are produced. It seems that the decomposition of the sugar (probably through some unknown intermediate product) takes place preferentially into aldehyde and formic acid, but that when this mode of decomposition is checked, possibly through accumulation of the decomposition products, other reactions take place; so, for example, in solutions containing a large quantity of hydroxyl ions, lactic acid is one of the chief products.

The following scheme represents diagrammatically the various possible courses of the sugar decomposition :



A detailed comparison of the purely chemical decomposition of the sugars with the alcoholic fermentation, the lactic acid fermentation, the acetic acid fermentation, and the formic acid fermentation shows that the latter processes are, so far as their end products are concerned, reproducible by agencies of a purely chemical nature. An enzyme is in fact only a catalytic agent of a special kind.

J. C. P.

#### The Liquefaction of Starch Powder and Starch Grains.

A. BOLDIN (*Compt. rend.*, 1906, 143, 511—512).—Prior to Fernbach and Wolfe (this vol., i, 804) the author has shown that potassium hydrogen phosphate prevents the liquefaction of starch paste (compare *Abstr.*, 1904, ii, 816), and in the present paper it is shown that whilst magnesium phosphate has a similar action, calcium phosphate does not render starch viscous, and if a solution of purified starch powder is heated in the presence of calcium sulphate or phosphate, it is saccharified to the extent of 33 per cent. Further, if the alkali hydrogen phosphates present in the starch granules are converted into calcium phosphate by the addition of calcium chloride, or into the corresponding di-hydrogen phosphate by the addition of acid, the solution obtained by boiling the starch grains is limpid and mobile and readily saccharified.

M. A. W.

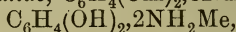
**Preparation of Methylamine from Ammonia and Methyl Sulphate.** JAMES BURMANN (*Bull. Soc. chim.*, 1906, [iii], 35, 801—803).—Commercial methyl sulphate is added in small portions at a time to excess of a 10 per cent. aqueous solution of ammonia cooled to  $-5^{\circ}$ . The product is then added to excess of a 30 per cent. aqueous solution of sodium hydroxide and the mixture distilled, the issuing gas being passed into hydrochloric acid (20 per cent.). On evaporating, the ammonium chloride separates first and the methylamine hydrochloride ultimately obtained is purified by recrystallisation from boiling absolute alcohol. The yield is about 35 per cent. of the theoretical.

T. A. H.

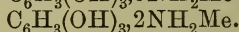
**Liquid Methylamine as a Solvent, and a Study of its Chemical Reactivity.** HARRY D. GIBBS (*J. Amer. Chem. Soc.*, 1906, 28, 1395—1422).—Liquid methylamine is a very good solvent for

organic compounds, being better than liquid ammonia and probably better than methyl alcohol. For inorganic compounds, however, it is not so good a solvent as liquid ammonia, is far inferior to water, and seems to be approximately equal to methyl alcohol. The solubilities of various organic and inorganic substances have been studied as well as the reactions which sometimes take place.

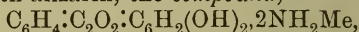
The hydrocarbons are generally very soluble and the solid members crystallise readily from the solutions. The alcohols and phenols are also readily soluble. The following additive compounds are described. The phenol compound,  $C_6H_5 \cdot OH, 2NH_2Me$ , melts at  $8.5-9.0^\circ$ . The  $\alpha$ -naphthol compound,  $C_{10}H_7 \cdot OH, 2NH_2Me$ , melts at about  $37^\circ$ . Quinol yields the compounds,  $C_6H_4(OH)_2, 8NH_2Me$ ,



and  $C_6H_4(OH)_2, NH_2Me$ , the last melting at  $105^\circ$ . Resorcinol gives the compounds,  $C_6H_4(OH)_2, 5NH_2Me$ ,  $C_6H_4(OH)_2, 2NH_2Me$ , and  $C_6H_4(OH)_2, NH_2Me$ , the last of which melts at  $95^\circ$ . Pyrogallol furnishes the compounds  $C_6H_3(OH)_3, 3NH_2Me$  and

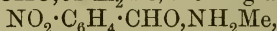


With phenolphthalein, the compound,  $C_6H_4 : C_2O_2 : (C_6H_4 \cdot OH)_2, 2NH_2Me$  is obtained, and with alizarin, the compound,



is produced. On evaporating a solution of picric acid in liquid methylamine, a substance is obtained which decomposes without melting at  $195^\circ$ . Thymol yields a crystalline substance melting at  $25^\circ$ .

Acetaldehyde and benzaldehyde are miscible with liquid methylamine. *m*-Nitrobenzaldehyde is readily soluble and gives the compounds,  $NO_2 \cdot C_6H_4 \cdot CHO, 6NH_2Me$ , melting at  $-9^\circ$ , and



which melts and decomposes at  $47^\circ$ .

Acetone, acetophenone, and carbamide dissolve readily in liquid methylamine. Benzil is also very soluble and yields a substance,  $COPh \cdot COPh, 2NH_2Me$ , which melts at about  $23^\circ$ . Quinone reacts with methylamine with development of heat and formation of a liquid which becomes successively green, purple and black. Anthraquinone is only slightly soluble.

The organic acids are generally very soluble, but in some cases insoluble methylamine salts are produced. The methylamine salts of several organic acids are described. The acetate melts at about  $80^\circ$ , the palmitate at  $62^\circ$ , the succinate at  $150^\circ$ , the tartrate at  $148^\circ$ , the benzoate at  $110-112^\circ$ , and the *o*-nitrobenzoate at  $128-129^\circ$ . Phthalic anhydride reacts with methylamine with development of heat and formation of a crystalline substance, which is probably methylamine methylphthalamate,  $NHMe \cdot CO \cdot C_6H_4 \cdot CO_2H, NH_2Me$ . The urate decomposes without melting.

Chloroform mixes with liquid methylamine in all proportions and slowly reacts with it to form methylcarbimide and methylamine hydrochloride. Ethylene bromide reacts with methylamine with formation of a crystalline substance, which melts at  $179^\circ$  and is probably dimethylethylenediamine hydrobromide. Bromobenzene and *p*-bromoacetanilide dissolve freely without change.

Nitromethane is miscible with liquid methylamine and yields a



crystalline compound,  $\text{CH}_3\cdot\text{NO}_2\cdot\text{NH}_2\text{Me}$ , which melts between  $-8.0^\circ$  and  $-7.5^\circ$ . Nitrobenzene, *m*-dinitrobenzene, *o*-nitrotoluene, 2:4-dinitrotoluene, and 2:4-dinitroaniline are very soluble. 2:4:6-Trinitroaniline yields a red, crystalline substance.

Galactose and dextrose are soluble in liquid methylamine and furnish compounds of the composition  $\text{C}_6\text{H}_{12}\text{O}_6\cdot 2\text{NH}_2\text{Me}$ . Sucrose is also readily soluble.

Acetamide, phenylhydrazine, amyl formate, pyridine, azobenzene, *m*-nitrobenzenesulphonamide, and benzenesulphonimide are very soluble in liquid methylamine. Diphenylketoxime dissolves readily and yields the compound,  $\text{CPh}_2\cdot\text{NOH}\cdot\text{NH}_2\text{Me}$ , which decomposes a little below  $140^\circ$ .

Gallein and cœrulein furnish the compounds  $\text{C}_{20}\text{H}_{12}\text{O}_7\cdot 3\text{NH}_2\text{Me}$  and  $\text{C}_{20}\text{H}_{10}\text{O}_6\cdot 2\text{NH}_2\text{Me}$ . Dichlorogallein and tetrachlorogallein yield products containing about 23 and 25 per cent. of methylamine respectively. Indigotin and rosaniline are readily soluble, whilst methyl orange is only slightly so.

The behaviour of a large number of inorganic salts with liquid methylamine is described. The sulphates are usually insoluble, whilst of the nitrates and haloids some are soluble and others insoluble. The following additive compounds are described:  $\text{CdI}_2\cdot 4\text{NH}_2\text{Me}$ ,  $\text{AgNO}_3\cdot 4\text{NH}_2\text{Me}$ , and  $\text{AgNO}_3\cdot 2\text{NH}_2\text{Me}$ . Bismuth chloride, calcium chloride, chromic chloride, lithium chloride, lithium nitrate, lead nitrate, mercury methyl chloride, mercuric iodide, and probably cuprous chloride, cupric sulphate, mercurous chloride, and mercuric cyanide also form products containing methylamine of crystallisation.

E. G.

**Compounds formed by the Action of Ammonia or Amines on Mercury Salts.** DANIEL STRÖMHOLM (*Arkiv Kem. Min. Geol.*, 1906, 2, No. 23, 1—25).—The author classifies the definite compounds formed by ammonia or amines with mercury salts as follows: (A) Those in which  $\text{Hg}:\text{X}=1:2$ ; these are regarded as ammonia compounds. (B) Those in which  $\text{Hg}:\text{X}$  is greater than  $1:2$ , and which are of the types: (1) with ammonia,  $\text{NH}_2\cdot\text{HgX}$ ,  $\text{Hg}\cdot\text{N}\cdot\text{HgX}$ , and  $\text{Hg}\cdot\text{N}\cdot\text{HgX} + \text{H}_2\text{O}$ ; (2) with primary amines,  $\text{NHR}\cdot\text{HgX}$  and  $\text{Hg}(\text{NR}\cdot\text{HgX})_2$ . Compounds of the last type have not previously been prepared, although references have been made in the literature to ammonia derivatives of this type; the existence of the latter, however, the author was unable to confirm.

Working under the same conditions as Köhler (*Abstr.*, 1880, 159, and *Ber.*, 1879, 12, 2321), the author was unable to obtain any of the three compounds of ethylamine and mercuric chloride described by this author. Instead, he obtained the compound  $\text{N}_2\text{Et}_2\text{Hg}_3\text{Cl}_2$  as a white, amorphous mass.

Other compounds prepared from amines are:  $\text{NHEt}_2\cdot\text{HgCl}_2$ , from diethylamine;  $\text{N}_2\text{Pr}_2\text{Hg}_3\text{Cl}_2$ , from propylamine;  $\text{N}_2\text{Me}_2\text{Hg}_3\text{Cl}_2$ , from methylamine. Compounds were also obtained from amylamine ( $\text{Hg}:\text{Cl}=1.15:1$ ) and benzylamine ( $\text{Hg}:\text{Cl}=0.97:1$ ).

The interaction of mercuric nitrate, ammonium nitrate, and

ammonia in varying proportions, gave the diammononitrate, aminonitrate, and nitrate of Millon's base,  $\text{NHg}_2\cdot\text{OH}$ . T. H. P.

**Preparation of Amino-alcohols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 173610).—By the action of ammonia or organic bases on the  $\beta$ -substituted dihalogen hydrins,  $\text{OH}\cdot\text{CR}(\text{CH}_2\text{X})_2$ , where X is a halogen, new alcohol bases are produced having the general formula  $\text{OH}\cdot\text{CR}(\text{CH}_2\cdot\text{NYZ})_2$ ; these substances or their derivatives are of therapeutic importance owing to their property of dissolving uric acid.

*Tetramethyldiaminodimethylethylcarbinol*,  $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NMe}_2)_2$ , prepared by heating  $\beta$ -ethyldichlorohydrin with aqueous dimethylamine at  $180^\circ$ , is a limpid oil boiling at  $87^\circ$  under 17 mm. pressure, which can be distilled under the ordinary pressure without decomposition; its *hydrochloride*,  $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NMe}_2)_2\cdot\text{HCl}$ , has a neutral reaction, and is a white, crystalline, hygroscopic substance. The hydriodide is also a well-defined salt.

*Diaminodimethylethylcarbinol*,  $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NH}_2)_2$ , obtained in a similar manner, boils at  $115^\circ$  under 16 mm. pressure, and is very soluble in water.

*Dianilinodimethylethylcarbinol*,  $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NHPh})_2$ , prepared by heating  $\beta$ -ethyldibromohydrin and aniline at  $200^\circ$ , is a yellow oil having an odour of quinoline and boiling at  $145\text{--}148^\circ$  under 17 mm. pressure.

*Tetramethyldiaminophenyldimethylcarbinol*,  $\text{OH}\cdot\text{CPh}(\text{CH}_2\cdot\text{NMe}_2)_2$ , formed by condensing  $\beta$ -phenyldichlorohydrin with aqueous dimethylamine at  $180^\circ$ , is a yellow oil with a basic odour; it boils at  $139\cdot5^\circ$  under 11 mm. pressure.

*Dipiperidyldimethylethylcarbinol*,  $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{C}_5\text{NH}_{10})_2$ , is a viscid, colourless oil boiling at  $174^\circ$  under 16 mm. pressure.

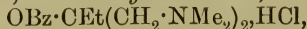
*Dimethylaminodiethylaminodimethylethylcarbinol*,  
 $\text{OH}\cdot\text{CEt}(\text{CH}_2\cdot\text{NMe}_2)\cdot\text{CH}_2\cdot\text{NEt}_2$ ,  
 is a colourless liquid boiling at  $107^\circ$  under 16 mm. pressure.

G. T. M.

**Preparation of Diaminoalkyl Esters.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 173631. Compare preceding abstract).—*Tetramethyldiaminodimethylethylcarbinyl benzoate*,



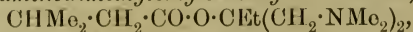
produced by the Schotten-Baumann reaction from tetramethyldiaminodimethylethylcarbinol, forms a *hydrochloride*,



separating in white crystals and melting at  $169^\circ$ .

*Tetramethyldiaminophenyldimethylcarbinyl benzoate hydrochloride*,  $\text{OBz}\cdot\text{CPh}(\text{CH}_2\cdot\text{NMe}_2)_2\cdot\text{HCl}$ , produced by benzoylating the corresponding carbinol with benzoyl bromide in pyridine and combining the resulting benzoate with hydrogen chloride (1 mol.), is a white, crystalline powder melting at  $187^\circ$ .

*Tetramethyldiaminodimethylethylcarbinyl isovalerate*,

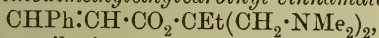


prepared by treating the corresponding carbinol with isovaleryl chloride and sodium hydroxide, is a colourless liquid boiling at  $137^\circ$

under 16 mm. pressure and having a faint aromatic and basic odour.

*Tetramethyldiaminodimethylethylcarbinyl ethyl carbonate*, obtained from the corresponding carbinol and ethyl chlorocarbonate, is a colourless oil boiling at 129° under 17 mm. pressure; the *hydrochloride* is a white, crystalline powder which melts at 160°.

*Tetramethyldiaminodimethylethylcarbinyl cinnamate*,



is a viscid, colourless oil; its *monohydrochloride* is a white, crystalline powder having a neutral reaction in aqueous solution. This salt produces an anæsthetic effect, lasting twice as long as that brought about by the same quantity of cocaine.

G. T. M.

**Copper and Nickel Salts of Certain Amino-acids.** ALESSANDRO CALLEGARI (*Gazzetta*, 1906, 36, ii, 63—67. Compare Bruni and Fornara, *Abstr.*, 1904, i, 855; 1905, i, 263; Ley, *Abstr.*, 1905, i, 175).—The *copper* salt of  $\beta$ -aminopropionic acid ( $\beta$ -alanine), prepared by warming the acid with freshly precipitated copper hydroxide, has the properties of an ordinary copper salt and not those of a cuprammonium derivative (*loc. cit.*); the cuprammonium or nickelammonium salts appear to be formed only from  $\alpha$ -amino-acids. *Copper aminosulphonate*,  $(\text{NH}_2\cdot\text{SO}_2\cdot\text{O})_2\text{Cu}\cdot 2\text{H}_2\text{O}$ , prepared by dissolving copper carbonate in an aqueous solution of aminosulphonic acid, forms microscopic, blue crystals and is an ordinary copper salt; the *nickel* salt,  $(\text{NH}_2\cdot\text{SO}_3)_2\text{Ni}\cdot 4\text{H}_2\text{O}$ , is similar. The copper salt of hydrazinecarboxylic acid (Stollé and Hofmann, *Abstr.*, 1905, i, 28) is apparently a cuprammonium salt, as it has the intense violet colour characteristic of such salts; it cannot be isolated, as it rapidly decomposes, giving metallic copper. The *nickel* salt,  $(\text{NH}_2\cdot\text{NH}\cdot\text{CO}_2)_2\text{Ni}$ , can be isolated, and is a nickelammonium salt; its solution is intensely blue and does not respond to the usual tests for nickel.

W. A. D.

**Optically Active  $\alpha\beta$ -Diaminopropionic  $\alpha$ - and  $\beta$ -Thioglyceric Acids.** CARL NEUBERG and ERICH ASCHER (*Chem. Centr.*, 1906, ii, 1119; from *Biochem. Zeit.*, 1906, 1, 380—382).—The racemic variety of  $\alpha\beta$ -diaminopropionic acid can be split into its optically active constituents by the fractional crystallisation of its salt with *d*-camphorsulphonic acid; in this way the dextro-variety can be obtained practically pure. The sulphate of the latter is converted by barium nitrite into *l*-glyceric acid, from which it follows that dextrorotatory  $\alpha\beta$ -diaminopropionic acid is in reality a *lævo* form. The *hydrochloride* of *l*-diaminopropionic acid is dextrorotatory; it forms a copper salt,  $(\text{C}_3\text{H}_7\text{O}_2\text{N}_2)_2\text{Cu}\cdot\text{H}_2\text{O}$ . When protein cystin is treated in sulphuric acid solution with barium nitrite, it is converted into  $\alpha\beta$ -thioglyceric acid which has  $[\alpha]_D - 10\cdot6^\circ$  (approx.); its *barium* salt,  $(\text{C}_3\text{H}_4\text{O}_3\text{S})_2\text{Ba}$ , has  $[\alpha]_D - 19\cdot08^\circ$ . A solution of the barium salt gives heavy precipitates with mercuric chloride, lead, or copper acetates. Zinc and hydrochloric acid reduce the disulphide to  $\beta$ -thioglyceric acid, a substance which, with lead, copper, or iron salts, gives colour reactions similar to those of cystein. In preparing the inactive  $\alpha\beta$ -diaminopropionic acid from  $\alpha\beta$ -dibromopropionic acid and ammonia, 10 per cent. of the dibromo-acid is



converted into *isoserine*. Cystin, on dry distillation, loses carbon dioxide, giving *diaminoethylene disulphide*, which was isolated in the form of a picrate. P. H.

**Reduction of Oximino-Esters. Synthesis of a New Leucine.** LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], 35, 965—969).—Most of the facts recorded in this paper have already been given (Abstr., 1905, i, 636).—When ethyl  $\alpha$ -oximino- $\beta$  methylvalerate is reduced with sodium amalgam in a cold alcoholic solution, only 35 per cent. of the theoretical yield of ethyl  $\alpha$ -amino- $\beta$ -methylvalerate is obtained, but a 60 per cent. yield may be secured by effecting the reduction with zinc dust and alcohol saturated with hydrogen chloride. From this amino-ester the corresponding acid (Ehrlich's *isoleucine*, Abstr., 1904, i, 560) may be obtained by agitating its solution in ether with a dilute aqueous solution of sodium hydroxide. The acid yields a *p*-toluenesulphonate which melts at 139°, and when warmed with formic acid (compare Fischer and Warburg, Abstr., 1906, i, 72) furnishes the formyl derivative,  $\text{CHMeEt}\cdot\text{CH}(\text{NH}\cdot\text{CHO})\cdot\text{CO}_2\text{H}$ , which crystallises from boiling water and melts at 121—122°. The amino-acid prepared in this way is racemic.

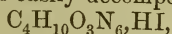
With benzoyl chloride in cooled pyridine solution, ethyl  $\alpha$ -aminoisohexanoate forms a *benzoyl* derivative, which crystallises from a mixture of alcohol and light petroleum, melts at 79°, and boils at 211° under 15 mm. pressure. T. A. H.

**Additive Compounds of Dicyanodiamide and Inorganic Salts.** HERMANN GROSSMANN and BERNHARD SCHÜCK (*Ber.*, 1906, 39, 3591—3593).—The compound  $\text{CuSO}_4\cdot 2\text{C}_2\text{H}_4\text{N}_4\cdot 4\text{H}_2\text{O}$ , formed by heating copper sulphate with dicyanodiamide in aqueous solution on the water-bath, is obtained as a light blue, thick, crystalline precipitate which becomes dark green when dried at 125°; the filtrate yields only green, basic products of varying composition. The compound  $\text{CdSO}_4\cdot 2\text{C}_2\text{H}_4\text{N}_4\cdot 2\text{H}_2\text{O}$  crystallises in short, colourless prisms, effloresces on exposure to air, and is more soluble in water than is the copper compound. The mercuric compound  $\text{HgCl}_2\cdot \text{C}_2\text{H}_4\text{N}_4$  crystallises in glistening, pointed needles. The copper and cadmium compounds belong to Werner's co-ordinated types  $(\text{MA}_6)_\text{X}_2$  and  $(\text{M}\cdot\frac{\text{A}}{\text{X}}_4)$ , whilst the mercuric compound is only incompletely co-ordinated. G. Y.

**Oxidation of Uric Acid in the presence of Ammonia.** GUSTAV DENICKE (*Annalen*, 1906, 349, 269—298).—*Iminoallantoin*,  $\text{C}_4\text{H}_7\text{O}_2\text{N}_5$ , obtained when finely divided uric acid, suspended in ammonium hydroxide at 0°, is oxidised by one atomic proportion of oxygen derived from potassium permanganate or ferricyanide, separates from hot water in elongated crystals, darkens at 210°, and carbonises at 295° without melting, is soluble in mineral acids, yields oxalic acid with warm potassium hydroxide, and in acid solution or by prolonged boiling with water is converted into allantoin. The resolution into its active components is not effected by tartaric acid.

When the oxidation is performed under similar conditions with

potassium ferricyanide (2 atoms of oxygen), crystals of a *substance*,  $C_4H_{10}O_3N_6$ , (*A*), are precipitated, whilst from the filtrate a *substance*,  $C_4H_8O_2N_6$ , (*B*), is obtained; the latter only is formed when the oxidation is effected with more concentrated ammonium hydroxide at the ordinary temperature. The substance *A* darkens at  $108^\circ$  and is carbonised at  $295^\circ$ , dissolves in cold water to an alkaline solution which decomposes by warming, and changes into *B* when digested with ammonium hydroxide. It is soluble in a small quantity of cold concentrated hydrochloric acid (parabanic acid is obtained by warming), and from the solution a *substance*,  $C_4H_5O_2N_5$ , separates; by saturating the solution with ammonia, oxaluric acid is obtained. With alcoholic hydrogen iodide at  $-7^\circ$ , an easily decomposable *hydriodide*,



is formed.

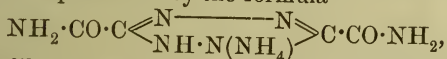
The substance *B* forms microscopic prisms, darkens at  $200^\circ$ , forms a neutral solution in water, and is decomposed by hydrochloric acid, yielding ultimately parabanic acid.

Both *A* and *B* are decomposed by potassium hydroxide, forming urea and a *substance* the composition of which approximates to that of di-iminoparabanic acid,  $C_3H_4ON_4$ ; this substance is a white powder which darkens at  $195^\circ$ , forms a crystalline *potassium* derivative, and by acids is converted into parabanic acid.

The evidence for the formulæ of these substances is discussed.

C. S.

**Pseudodiazacetamide.** THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1906, 39, 3410—3437. Compare Curtius, *Abstr.*, 1885, 883; Hantzsch and Silberrad, *Abstr.*, 1900, i, 261; Silberrad, *Trans.*, 1902, 81, 601).—The ammonium salt of pseudodiazacetamide is represented by the formula



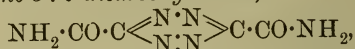
and is most readily prepared by the action of liquid ammonia on ethyl diazoacetate; no diazoacetamide is formed, and only a very small amount of bisdiazacetamide, which is readily removed. When warmed with water, pseudodiazacetamide yields one-third of its nitrogen in the gaseous form, one-third as hydrazine, which was estimated as benzylideneazine, and the remainder as glyoxylamide, which was isolated in the form of its phenylhydrazone (Krückeberg, *Abstr.*, 1894, i, 369). Carbon dioxide and oxalic acid do not appear to be formed, although both are produced when pseudodiazacetamide is washed with dilute acids.

The *azine* of *glyoxylamide*,  $NH_2 \cdot CO \cdot CH : N : N : CH \cdot CO \cdot NH_2$ , is obtained as an intermediate product when pseudodiazacetamide is warmed with water at  $60-70^\circ$  in small quantities until nitrogen ceases to be evolved and the solution cooled to  $0^\circ$ . It crystallises in small, pale yellow needles, melts at  $202^\circ$ , is soluble in warm water, but insoluble in alcohol or ether, and is readily hydrolysed, even in the cold, by dilute acids.

Pseudodiazacetamide is converted into bisdiazacetamide when

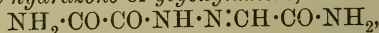
warmed with dilute sodium hydroxide solution, more slowly with the cold alkali, and also when warmed with ammonium hydroxide.

When an aqueous solution containing the ammonium salt of pseudo-diazoacetamide and sodium nitrite is acidified, a bluish-red precipitate of 1:2:4:5-tetrazine-3:6-dicarboxylamide,



is obtained. It is insoluble in all ordinary solvents, and when heated turns brown at 210° and is quite black at 280°. When warmed with water, nitrogen is evolved and the colour disappears. The same amide may be obtained by the oxidation of bisdiazacetamide with nitric acid; when reduced with hydrogen sulphide, it yields bisdiazacetamide.

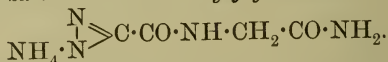
The *oxamic acid hydrazone* of glyoxylamide,



is obtained when tetrazinedicarboxylamide is boiled with water. It forms a pale yellow, crystalline powder, is insoluble in all ordinary solvents, turns brown at 270°, but is not molten at 300°, and when boiled with dilute sulphuric acid yields semioxamazide (Kerp and Unger, Abstr., 1897, i, 270) together with glyoxylic acid.

The acid previously obtained by Hantzsch and Lehmann (Abstr., 1901, i, 132) and termed bisazoxyacetic acid is now shown to be 1:2:4:5-tetrazine-3:6-dicarboxylic acid. J. J. S.

**Action of Ammonia on Ethyl Diazoacetyl glycine.** (*iso-Diazoacetyl aminoacetic Acid*). II. THEODOR CURTIUS and JAMES THOMPSON (*Ber.*, 1906, 39, 3398—3409).—The product previously (this vol., i, 404) described as an azomethane derivative is shown to be the *ammonium salt* of *isodiazoacetyl glycinamide*,



This ammonium salt is stable, and does not lose ammonia when kept, but is strongly dissociated in aqueous solution; with cold aqueous hydrochloric acid, it gives up 1 mol. of ammonia, and with hot concentrated acid or alkali 2 mols. The ammonium salt reacts with benzoyl chloride and sodium hydrogen carbonate solution, yielding *benzoylisodiazoacetyl glycinamide*,  $\text{N}_2\text{H} : \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{COPh}$ , which crystallises from acetone in slender, colourless needles and melts and decomposes at 185°. The corresponding *acetyl* derivative,  $\text{C}_6\text{H}_5\text{O}_2\text{N}_4$ , crystallises from alcohol in colourless needles and melts and decomposes at 158°. When boiled with water or alcohol, it is hydrolysed. The *silver* salt,  $\text{N}_2\text{Ag} : \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , obtained by precipitating a solution of the ammonium salt with silver nitrate, forms slender needles, and may be recrystallised from hot water. *iso-*

*Diazoacetyl glycinamide*,  $\text{N} \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , obtained by suspending the silver salt in water, passing in hydrogen sulphide, and evaporating the clear solution under reduced pressure, forms glistening prisms melting and decomposing at 154—155°. It is hygroscopic, and explodes when rapidly heated. It dissolves readily in water, sparingly



in alcohol, and is insoluble in ether, acetone, or chloroform. Its aqueous solution is decidedly acid and decolorises bromine water; when heated with concentrated hydrochloric acid it yields nitrogen (1 mol.) and ammonia (1 mol.). It yields the same benzoyl and acetyl derivatives as are obtained from the ammonium salt. When the ammonium salt is heated with concentrated hydrochloric acid at 130—140° it yields nitrogen, chloroacetic acid, and glycollic acid. When boiled with normal sodium hydroxide solution for an hour, evaporated under reduced pressure, and decomposed at 0° with the theoretical amount of concentrated hydrochloric acid, it yields *isodiazoacetylaminooacetic acid*,  $\text{N}=\text{N} \cdot \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , in the form of a white, crystalline precipitate, readily soluble in warm water, from which it crystallises in anisotropic, rhombic prisms. The same compound is formed by hydrolysing the ester with sodium hydroxide solution. It possesses both acid and basic properties. The *hydrochloride* forms a crystalline mass melting at 151°. The free acid when slowly heated decomposes at 169—170°.

A considerable amount of potassium cyanide is formed when ammonium *isodiazoacetyl*glycinamide is fused with potassium hydroxide.

J. J. S.

**Remarkable Formation of Alkyl Derivatives of Mercury.** JULIUS TAFEL (*Ber.*, 1906, 39, 3626—3631).—Considerable amounts of mercury *sec.*-butyl are formed when methyl ethyl ketone is reduced electrolytically in the presence of mercury cathodes. The maximum yields are obtained at a temperature of 45—50°. The cathode liquid consists of the ketone with some thirteen times its weight of 30 per cent. sulphuric acid, and a voltage of 7.6 to 8.4 for a current of 25 amperes is employed. After some two hours, the amount of crude mercury compound is 1.3 times the weight of ketone used. After several distillations in high vacua, the *mercury sec.-butyl*,  $\text{Hg}(\text{C}_4\text{H}_9)_2$ , is obtained as a colourless oil boiling at 46° under very low pressures, and a considerable residue of another mercury compound in the form of a yellow oil is left. The mercury butyl boils at 91—93° under 15 mm. pressure, and readily reacts with iodine, yielding *sec.*-butyl iodide and mercury butyl iodide.

J. J. S.

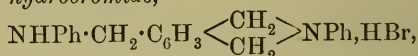
**The Study of Hydroaromatic Substances.** EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, jun., MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Rep.*, 1905, 153).—A report on the production of hydroaromatic substances from the aromatic hydrocarbons, phenols, amines, ketones, and acids. Reference is also made to the nature of double linkings.

G. T. M.

**Fluoro-aromatic Compounds.** ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1906, [ii], 25, 330—333).—*o*- and *p*-Fluoroacetanilides prepared by reducing the crude fluoronitrobenzene (M. Holleman, *Abstr.*, 1905, i, 424) and acetylating the product, can be separated by repeated fractional crystallisation from benzene and light petroleum; *o*-fluoroacetanilide melts at 80°, and *p*-fluoroacetanilide at 150°.

*p*-Fluorotoluene (Holleman and Beckman, Abstr., 1904, i, 232) freezes in a mixture of solid carbon dioxide and alcohol, whilst the ortho- and meta-isomerides remain liquid. "Fluoro-saccharin" (De Roode, Abstr., 1891, 1226) can be prepared from *p*-fluorotoluene by converting it into *p*-fluorotoluenesulphonic chloride, which boils at 145—150° under 20 mm. pressure and yields the corresponding sulphonamide melting at 140° (De Roode gives 155°) on treatment with ammonium carbonate; this can be oxidised by potassium permanganate to "fluoro-saccharin" melting at 200°. M. A. W.

**Action of Bromine on  $\psi$ -Cumene.** ROBERTO CIUSA (*Gazzetta*, 1906, 36, ii, 90—93. Compare Schramm, Abstr., 1886, 451; Hjelt and Gadd, *ibid.*, 615).—*Tri- $\omega$ -bromocumene*,  $C_6H_3(CH_2Br)_3$ , obtained by adding bromine (3 mols.) to  $\psi$ -cumene exposed to direct sunlight, and subsequently heating at 160°, crystallises from light petroleum in white, lustrous needles and melts at 154°. Its structure follows from its yielding with aniline in alcoholic solution 6-*anilinomethyl-2-phenyl-dihydroisoindole hydrobromide*,



which crystallises from light petroleum and melts at 132°; the base,  $C_{21}H_{20}N_2$ , also crystallises from light petroleum and melts at 128°.

W. A. D.

**Derivatives of *tert.*-Butylbenzene.** EYVIND BÆDTKER (*Bull. Soc. chim.*, 1906 [iii], 35, 825—836. Compare Abstr., 1904, i, 801).—*p*-Chloro-*tert.*-butylbenzene, obtained by condensing chlorobenzene with *tert.*-butyl chloride or isobutyl chloride in presence of aluminium chloride, is a limpid liquid with an aromatic odour, boils at 211° (corr.) under 759 mm. pressure, has a sp. gr. 1.0075 at 18.5°/4° and  $n_D$  1.51230 at 20°. On oxidation with chromic acid it furnishes *p*-chlorobenzoic acid. It dissolves in fuming nitric acid, yielding a mixture of 4-chloro-2:3-dinitro-*tert.*-butylbenzene and 4-chloro-3:5-dinitro-*tert.*-butylbenzene. The first of these is a yellow, crystalline powder and melts at 94—95°, and the second crystallises in hexagonal tablets, large, prismatic needles, or small prismatic grains and melts at 116—117°. When isobutyl chloride is condensed with bromobenzene in presence of aluminium chloride, the principal fraction is a *product* boiling at 225—226° at atmospheric, or at 110—111° under 15 mm. pressure, and only a small quantity of *p*-bromo-*tert.*-butylbenzene is obtained. This boils at 232—233° (compare Schramm, Abstr., 1889, 127). The nature of the fraction boiling at 225—226° has not been definitely ascertained. On oxidation with chromic acid it furnishes *p*-bromobenzoic acid, and on solution in fuming nitric acid yields a mixture of 4-bromo-2:3-dinitro-*tert.*-butylbenzene and 4-bromo-3:5-dinitro-*tert.*-butylbenzene. The first of these is a yellow, crystalline powder and melts at 92—93°, and the second forms slender, almost colourless, needles and melts at 136°.

*p*-Iodo-*tert.*-butylbenzene, obtained together with di-iodobenzene (Dumreicher, Abstr., 1883, 53) when isobutyl chloride is condensed with iodobenzene in presence of ferric chloride, boils at 253—254°

(corr.) under 766 mm. pressure, has a sp. gr. 1.4392 at 14°/4°, and  $n_D$  1.57076 at 20°, and does not liberate iodine on exposure to light (compare Pahl, Abstr., 1884, 1009, and Bialobrzewski, *ibid.*, 1897, i, 514). On oxidation with chromic acid, it yields *p*-iodobenzoic acid (m. p. 236°; compare Glassner, Abstr., 1875, 888). On nitration, it liberates some iodine and furnishes (a) 4-iodo-2 : 3-dinitro-*tert*-butylbenzene, which crystallises in lemon-yellow leaflets and melts at 110—111°, and (b) a substance forming colourless prismatic crystals, melting at 243° which may be a di-iodonitrobutylbenzene. When the parent substance is treated with a great excess of fuming nitric acid *p*-iodonitrobenzene is formed.

When *isobutyl* chloride is condensed with cumene in presence of aluminium chloride, *tert*-butylbenzene, *p*-di-*tert*-butylbenzene and propyl chloride are produced. An attempt to separate the constituents of this mixture by Radziewanowski's process (Abstr., 1895, i, 129) gave only a tarry product, which boiled above 300° and decomposed.

When *isoamyl* chloride is condensed with *tert*-butylbenzene in presence of aluminium chloride, *p*-di-*tert*-butylbenzene is produced and the *isoamyl* chloride can be recovered unaltered (compare Baur, Abstr., 1894, i, 445). The hydrocarbon, when dissolved in fuming nitric acid, furnishes 2 : 6-dinitro-1 : 4-di-*tert*-butylbenzene, which crystallises from boiling alcohol in slender, colourless needles and melts at 190—191° (corr.). Indications of the presence of an *o*-dinitro-derivative in the mother liquors from the crystallisation of the *m*-dinitro-derivative were obtained.

The dinitro-derivatives obtained from *p*-dibutylbenzene by Verley (Abstr., 1899, i, 424) and Baur (Abstr., 1894, i, 445) are probably impure.

T. A. H.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Rep.*, 1905, 103).—A report on the transformation of symmetrically trisubstituted aromatic nitroamines and diazonium hydroxides and on the action of light on solutions of certain diazonium salts.

G. T. M.

Combination of Magnesium Bromide with Certain Amines. VIII. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 5).—Aniline reacts with magnesium bromide with development of much heat, giving three compounds. The equilibrium curve of the system magnesium bromide-aniline consists of three branches, representing (1) the solubility of the compound,  $MgBr_2 \cdot 6NH_2Ph$  in aniline and ending at 103°; (2) the solubility of the compound  $MgBr_2 \cdot 4NH_2Ph$  and ending at 237°; (3) probably the compound  $MgBr_2 \cdot 2NH_2Ph$ , or  $MgBr_2 \cdot NH_2Ph$ , but owing to the setting in of decomposition, the investigation could not be carried beyond 250—260°. Phenylhydrazine also gives the compound  $MgBr_2 \cdot 6N_2H_3Ph$ , and its solubility curve corresponds closely with that of the aniline compound in aniline. The first curve ends at 99°, but owing to decomposition



the second was only observed up to 200°. It probably corresponds with the compound  $\text{MgBr}_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$ . Z. K.

**Cyanoacetylchloroanilines and the corresponding Oxamic Acids.** GALEAZZO PICCININI and A. DELPIANO (*Atti R. Accad. Sci. Torino*, 1906, 41, 1005—1018).—The three chloroanilines react with ethyl cyanoacetate yielding the corresponding chloro-derivatives of cyanoacetylaniline:  $\text{NH}_2 \cdot \text{C}_6\text{H}_4\text{Cl} + \text{CN} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} = \text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl} + \text{Et} \cdot \text{OH}$ .

*m*-Chlorocyanoacetylaniline,  $\text{C}_9\text{H}_7\text{ONCl}$ , prepared from *m*-chloroaniline and ethyl cyanoacetate, crystallises from aqueous alcohol in white, nacreous plates melting at 142° (corr.), dissolves readily in acetone and sparingly in ether or benzene, and is hydrolysed either by dilute alkali solution or, more slowly, by boiling with water.

*o*-Chlorocyanoacetylaniline crystallises from aqueous alcohol in small, colourless prisms or slender, silky needles melting at 125° and resembles the corresponding meta-compound in its behaviour towards solvents and hydrolytic agents.

*p*-Chlorocyanoacetylaniline crystallises from aqueous alcohol in shining, colourless prisms which aggregate in the form of plates having a silvery lustre; it melts at 204° and behaves towards solvents and hydrolysis like its isomerides.

When oxidised by means of a large excess of permanganate, these compounds yield, almost quantitatively, the corresponding chlorophenyl-oxamic acids, according to the equation:  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CN} + \text{O}_2 = \text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H} + \text{HCN}$ .

*p*-Chlorophenylloxamic acid,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , crystallises from absolute or aqueous alcohol with 1Et·OH in colourless prisms which melt at 190—191° and effloresce in the air; it dissolves readily in acetone and sparingly in chloroform or benzene. The *potassium*, *silver*, *barium*, *ferric*, *mercurous*, and *lead* salts are described.

*o*-Chlorophenylloxamic acid crystallises with  $\text{H}_2\text{O}$  from aqueous alcohol in colourless, prismatic needles and melts at 93—95°; the anhydrous acid melts at 136—137°. The *potassium*, *silver*, *calcium*, *barium*, *copper*, and *mercurous*, *lead*, and *ferric* salts are described.

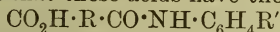
*m*-Chlorophenylloxamic acid crystallises from water with  $1\frac{1}{2}\text{H}_2\text{O}$  in shining needles melting at 90—100°, whilst the anhydrous acid melts at 144—145°; the acid dissolves much more readily than its isomerides in water and is soluble in 95 per cent. alcohol or acetone and sparingly so in benzene or chloroform. The *potassium* salt forms nacreous, anhydrous leaflets.

These three acids exhibit a strong acid reaction in aqueous solution and are monobasic towards alkali hydroxides, using phenolphthalein as indicator. T. H. P.

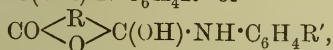
**Action of Phenylcarbimide on certain Phenylamic Acids.** GINO ABATI and PAOLO GALLO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 291—299).—The authors have examined the behaviour of phenylcarbimide towards solutions, in non-dissociating solvents, of phenylphthalamic, *p*-tolylphthalamic, *d*-*cis*-phenylcamphoramic and *p*-ethoxyphenylmaleinamic acids. With the exception of the phenyl-

camphoramic acid, all the acids are resolved into the corresponding anhydrides and aniline, the latter combining with the phenylcarbimide to form diphenylcarbamide.

This result indicates that these acids have the structure



rather than  $\text{CO}_2\text{H}\cdot\text{R}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{R}'$  or



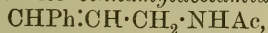
since the last two formulæ contain an alcoholic hydroxyl, which would be capable of reacting with the phenylcarbimide. The non-reactivity of *d-cis*-phenylcamphoramic acid with phenylcarbimide points

to its having the constitution  $\begin{matrix} \text{R}\cdot\text{CO} \\ | \\ \text{C}\cdot\text{O}\cdot\text{O} \end{matrix} \text{NH}_2\cdot\text{C}_6\text{H}_4\text{R}'$ .

In the cases of the above acids which react with phenylcarbimide, a deep yellow substance, readily soluble in ether, is formed in amount too small to allow of its investigation.

T. H. P.

**Cinnamylamine ("Styrylamine") Bases and their Relation to Ephedrine and  $\psi$ -Ephedrine.** [ERNST SCHMIDT] and HERMANN EMDE (*Arch. Pharm.*, 1906, 244, 269—299).—Cinnamylamine hydrochloride (E. Schmidt and Flaecher, *Abstr.*, 1905, i, 371) melts at 236°; the *aurichloride* and *mercurichloride* melt at 138—139° and 189° respectively. When the amine is boiled with excess of acetyl chloride it is converted into *cinnamylacetamide*,



which melts at 87.5°. It reacts with methyl iodide in methyl-alcoholic solution at the ordinary temperature; quaternary *cinnamyltrimethylammonium iodide*, melting at 178°, is practically the only product, but much of the amine remains unchanged; the corresponding quaternary *aurichloride* and *platinichloride* melt at 185° and 232—234° respectively.

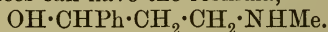
Cinnamyltrimethylamine (*Abstr.*, 1905, i, 370), *aurichloride*, *platinichloride*, *mercurichloride*, ( $\text{C}_{12}\text{H}_{18}\text{N}$ )<sub>2</sub>HgCl<sub>4</sub>,  $\frac{1}{2}\text{HgCl}_2$ , and *picrate* (not analysed) melt at 185°, 228—230°, 171°, and 159° respectively. With methylamine in alcoholic solution at the ordinary temperature cinnamyl chloride in part condenses to form *cinnamylmethylamine hydrochloride*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NHMe}\cdot\text{HCl}$ ; this and the corresponding *platinichloride*, *aurichloride*, *mercurichloride*,  $\text{C}_{10}\text{H}_{13}\text{N}\cdot\text{HHgCl}_3$ , and *picrate* (not analysed) melt at 151.5°, 212°, 103°, 166°, and 147° respectively. When cinnamyl chloride is warmed with pyridine, *cinnamylpyridine hydrochloride*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_4\cdot\text{HCl}$ , is formed; the corresponding *platinichloride*, *aurichloride*, and *picrate* (not analysed) melt at 220—222°, 101.5°, and 146° respectively.

Cinnamyltrimethylamine hydrochloride does not yield additive compounds with hydrogen bromide or iodide in aqueous solution, neither does cinnamylamine hydrochloride take up hydrogen when treated in aqueous alcoholic solution with sodium amalgam. Cinnamyltrimethylamine hydrochloride, however, in aqueous solution is attacked by sodium amalgam: it is decomposed almost quantitatively into  $\alpha$ -phenylpropylene,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_3$ , and trimethylamine hydrochloride, so that the

reaction can be used advantageously for the preparation of  $\alpha$ -phenylpropylene.

Neither cinnamylamine nor cinnamylmethylamine hydrochloride forms a chlorohydrin when treated with hypochlorous acid (aqueous sodium hypochlorite). Cinnamyltrimethylamine hydrochloride does form a *chlorohydrin*, presumably  $\text{OH}\cdot\text{CHPh}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$ , of which the *platinichloride* and *aurichloride* melt respectively at  $210\text{--}212^\circ$  and  $130\text{--}132^\circ$ ; the yield is not quantitative, however. This chlorohydrin is hardly affected by zinc and dilute sulphuric acid, but sodium amalgam does remove the chlorine, forming a quaternary ammonium base,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$ , of which the *aurichloride* and *platinichloride* melt at  $103^\circ$  and  $216\text{--}218^\circ$  respectively (a little of this base is formed when cinnamyltrimethylamine chloride is treated with aqueous hydrogen iodide).

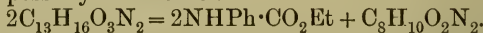
As this quaternary base is not identical with either of those prepared by the methylation of ephedrine and  $\psi$ -ephedrine respectively, neither of the latter substances can have the formula,



C. F. B.

**Condensation of Ethyl Acetoacetate and Phenylcarbamide.** WALTHER KIESSLING (*Annalen*, 1906, 349, 299—323).—Phenylcarbamide, unlike carbamide, thiocarbamide, or guanidine, condenses with ethyl acetoacetate in the presence of ether, to form not ethyl phenyluraminocrotonate (compare Behrend and Meyer, *Abstr.*, 1901, i, 136), but a yellow oil having the composition  $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2$  (compare Behrend, *Abstr.*, 1886, 443), the most suitable temperature being  $133\text{--}134^\circ$ . The oil, the mean molecular weight of which by the ebullioscopic method is 174.7, is decomposed by cold 5 per cent. hydrochloric acid or by alcohol, giving a yield of ethyl phenylcarbamate in accordance with the equation:  $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2 + 2\text{H}_2\text{O} = \text{NHPh}\cdot\text{CO}_2\text{Et} + \text{NH}_3 + \text{CO}_2 + \text{COMe}_2$ ; the carbamate is also obtained by inoculating the oil at  $0^\circ$  with a crystal of the ester.

For these reasons, the substance is regarded as an easily dissociable compound or possibly a mixture:



The hypothetical substance,  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$ , has not been isolated, but is regarded as containing the skeleton,  $\begin{array}{c} \text{MeC}\cdot\text{C}\cdot\text{CO} \\ \text{MeC}\cdot\text{C}\cdot\text{CO} \end{array}$  since the yellow oil and phenylhydrazine yield Knorr's bisphenylmethylpyrazolone.

Methylcarbamide reacts with ethyl acetoacetate at  $125\text{--}127^\circ$  in the presence of ether to form a *substance* which has the composition, but not the properties of ethyl methylaminocrotonate,  $\text{C}_7\text{H}_{13}\text{O}_2\text{N}$ .

Diphenylcarbamide, ethyl acetoacetate, and ether react at  $154^\circ$  to form a reddish-brown oil (compare Behrend, *Annalen*, 1886, 233, 11). This substance  $\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_2$  has a mean molecular weight 209, forms bisphenylmethylpyrazolone with phenylhydrazine, and when warmed with hydrochloric acid or alcohol yields ethyl phenylcarbamate. It may be a mixture of ethyl phenylcarbamate and the substance derived from the hypothetical  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$ , containing 2Ph in the place of hydrogen:  $2\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_2 = 2\text{C}_9\text{H}_{11}\text{O}_2\text{N} + \text{C}_8\text{H}_8\text{Ph}_2\text{O}_2\text{N}_2$ . C. S.



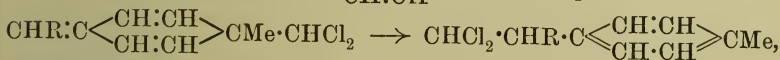
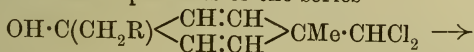
**Chlorinated Alcohols [Phenols] of the Dihydrobenzene Series and their Transformation Products.** KARL AUWERS (*Ber.*, 1906, 39, 3748—2757. Compare Auwers and Keil, *Abstr.*, 1903, i, 620; 1904, i, 26; Auwers and Hessenland, *Abstr.*, 1905, i, 434).—The product  $C_9H_{12}OCl_2$ , obtained with magnesium methyl iodide by Grignard's reaction from 1-keto-2-methyl-2-dichloromethyl-1:2-dihydrobenzene, is an oil which boils at 112—114° under 9 mm. or at 121—122·5° under 13 mm. pressure, and has a sp. gr. 1·202 at 20°/4°,  $n_D$  1·5023 at 19°, and a mol. refraction showing the presence of one double linking. The substance is extremely stable towards dehydrating agents, and is probably an oxide formed by intramolecular change from the tertiary alcohol constituting the product of the Grignard synthesis. When treated with concentrated sulphuric acid, it changes gradually into an *isomeride*, which forms stout crystals, melts at 40—41°, boils at 141—143° under 9 mm. pressure, and has a sp. gr. 1·2254 at 23·5°/4° or 1·2074 at 45°/4°,  $n_D$  1·51419 at 46°, and a mol. refraction pointing to the presence of a ketone with one double linking; the coefficient of dispersion is slightly greater than for the oxide.

The product,  $C_{10}H_{14}OCl_2$ , formed with magnesium ethyl iodide by Grignard's synthesis from 1-keto-2-methyl-2-dichloromethyl-1:2-dihydrobenzene, is an oil, which boils at 130—131° under 9 mm. pressure, has a sp. gr. 1·1860 at 20°/4° or 1·1833 at 24°/4°,  $n_D$  1·50251 at 20° or 1·50019 at 24°, resembles the methyl derivative in its stability towards dehydrating agents, and yields an oily *isomeride* on treatment with concentrated sulphuric acid.

All the preceding substances are more or less easily attacked by alkali hydroxides, being converted into chlorinated or non-chlorinated unsaturated acids, and finally into unsaturated hydrocarbons.

In the *para*-series, the derivatives of *as-o*-xylenol, *as-m*-xylenol, and *ψ*-cumenol behave in the same manner as the derivatives of the simpler *para*-substituted phenols.

The labile intermediate products of the series



are *para*-derivatives of alkylidene 1:4-dihydrobenzenes and are isomeric with the final benzene derivatives; these substances, termed by the author "semibenzenes," have mol. refractions higher than the calculated, and abnormally high coefficients of dispersion as compared with the normal dispersions of the aromatic series.

The relation of these facts to the constitution of the semibenzenes is discussed.

G. Y.

**Phenyl Chlorothiocabonates.** HENRI RIVIER (*Bull. Soc. chim.*, 1906, [iii], 35, 837—843).—*Phenyl chlorothioncarbonate*,  $CSCl \cdot OPh$ , obtained by the action of sodium phenoxide on thiocarbonyl chloride dissolved in chloroform, is a bright yellow liquid with a sharp odour, boils at 91° under 10 mm. and at 100° under 15 mm. pressure, crystallises at -0·5°, and has a sp. gr. 1·283 at 15°/4°. When dissolved in

alcohol it decomposes, slowly in the cold, or immediately at  $100^{\circ}$ , forming *phenyl ethyl thioncarbonate*,  $\text{OEt}\cdot\text{CS}\cdot\text{OPh}$ . This is a colourless liquid, with a pleasant ethereal odour, has a sp. gr.  $1\cdot135$  at  $15^{\circ}/4^{\circ}$ , and boils at  $124^{\circ}$  under 12 mm. and at  $130^{\circ}$  under 17 mm. pressure. Sodium phenoxide converts phenyl chlorothioncarbonate into diphenyl thioncarbonate, and some of the latter is formed as a by-product in the primary reaction (compare Eckenroth and Kock, Abstr., 1894, i, 408). Phenyl chlorothioncarbonate reacts with thiophenol or, better, with the lead derivative of the latter to form *diphenyl dithiocarbonate*,  $\text{SPh}\cdot\text{CS}\cdot\text{OPh}$ , which forms golden-yellow prisms and melts at  $51^{\circ}$ . Ammonia solution in excess decomposes phenyl chlorothioncarbonate, forming phenol and ammonium thiocyanate and chloride, but with smaller quantities *phenyl thioncarbamate*,  $\text{NH}_2\cdot\text{CS}\cdot\text{OPh}$ , may be obtained. This separates from alcohol in flat, colourless needles and melts at  $132\text{--}132\cdot5^{\circ}$ . With methylamine, *phenyl methylthioncarbamate*,  $\text{NHMe}\cdot\text{CS}\cdot\text{OPh}$ , is produced as an oil which could not be obtained pure. With aniline, *phenyl phenylthioncarbamate*,  $\text{NHPh}\cdot\text{CS}\cdot\text{OPh}$ , is obtained. This crystallises from alcohol in small, colourless needles and decomposes when heated, forming a liquid mixture of phenol and phenylthiocarbimide.

The author agrees with Orndorff and Richmond (Abstr., 1900, i, 156) that the substance described by Dixon (Trans., 1890, 57, 268); Snape (Trans., 1896, 69, 98), and Eckenroth and Kock (*loc. cit.*) as phenyl phenylthioncarbamate was probably thiocarbanilide. *Phenyl dimethylthioncarbamate*,  $\text{NMe}_2\cdot\text{CS}\cdot\text{OPh}$ , obtained by the action of dimethylamine on phenyl chlorothioncarbonate, separates from ether in colourless prisms and melts at  $30\text{--}30\cdot4^{\circ}$ . *Phenyl phenylmethylthioncarbamate*, similarly obtained from methylaniline, forms colourless crystals and melts at  $104^{\circ}$ . Phenyl phenylethylthioncarbamate melts at  $69\cdot2^{\circ}$  (compare Billeter and Strohl, Abstr., 1888, 364). The last three substances are less readily decomposed by alkalis, water, or alcohol than their analogues described above.

T. A. H.

**Preparation of 2-Nitro-6-amino-4-acetaminophenol.** LEOPOLD CASSELLA & Co. (D.R.-P. 172978). When 4-acetaminophenol is strongly nitrated two nitro-groups are introduced into the ortho-positions with respect to the hydroxyl group. The dinitro-compound when converted into its sodium derivative and reduced by warming with dilute aqueous sodium sulphide, gives rise to 2-nitro-6-amino-4-acetaminophenol,  $\text{NHAc}\cdot\text{C}_6\text{H}_2(\text{NO}_2)(\text{NH}_2)\cdot\text{OH}$ , which crystallises from alcohol in brownish-red needles and melts at  $190^{\circ}$ . This substance is feebly basic; its *hydrochloride*, which crystallises in yellow needles, being dissociated by water; with nitrous acid, it yields an orange-yellow *diazo*-derivative.

G. T. M.

**Preparation of Diaryl Sulphides.** FERD. MAUTHNER (*Ber.*, 1906, 39, 3593—3598). Compare this vol., i, 421; Bourgeois, Abstr., 1896, i, 17).—A number of diaryl sulphides, of which those described below are new, have been prepared by the action of aryl iodides on sodium arylmercaptides in presence of copper powder. This reaction constitutes a general method for the preparation of the diaryl sulphides.

*o-Tolyl-m-tolyl sulphide*,  $C_{14}H_{14}S$ , from *o*-thiocresol and *m*-iodotoluene, is a colourless, odourless oil, which boils at  $170^\circ$  under 11 mm. pressure. *Di-m-tolyl sulphide*, from *m*-thiocresol and *m*-iodotoluene, is a colourless oil which boils at  $174^\circ$  under 12 mm. pressure.

*o-Methoxydiphenyl sulphide*,  $C_{13}H_{12}OS$ , from thiophenol and *o*-iodoanisole, is a colourless oil which has an unpleasant, aromatic odour, and boils at  $196^\circ$  under 11 mm. pressure.

*m-Thioanisole*,  $C_7H_8OS$ , prepared by diazotisation of *m*-anisidine and treatment of the solution with potassium xanthate at  $80-90^\circ$ , boils at  $224-225^\circ$  (corr.). *Di-m-methoxyphenyl sulphide*,  $C_{14}H_{14}O_2S$ , is a colourless oil which boils at  $214-215^\circ$  under 10 mm. pressure.

As the iodonitrobenzenes are unstable, the corresponding bromides are employed in the preparation of nitro-derivatives of diphenyl sulphide.

*o-Nitrodiphenyl sulphide*,  $C_{12}H_{11}O_2NS$ , crystallises from light petroleum in long, yellow needles, melts at  $77^\circ$ , and gives a green coloration with concentrated sulphuric acid. On reduction with stannous chloride and hydrochloric acid, it yields *o-aminodiphenyl sulphide*, which is obtained as a colourless oil; the *sulphate*,  $C_{12}H_{13}O_4NS_2$ , forms long needles and is decomposed by water. The *acetyl* derivative,  $C_{14}H_{13}ONS$ , crystallises in colourless needles and melts at  $86^\circ$ .

*o-Nitrophenyl o-tolyl sulphide*,  $C_{12}H_{11}O_2NS$ , from *o*-thiocresol and *o*-bromonitrobenzene, crystallises from light petroleum in yellow needles and melts at  $86-87^\circ$ , and gives a green coloration with concentrated sulphuric acid.

G. Y.

**Aromatic Sulphine Bases. II.** FRIEDRICH KEHRMANN and ALFRED DUITENHÖFER (*Ber.*, 1906, 39, 3559—3560. Compare this vol., i, 83).—Aryldimethylsulphine salts are formed by heating the aromatic mercaptans with an excess of methyl sulphate at  $100^\circ$ ; the methyl mercaptide formed in the first stage of the reaction combines with methyl sulphate, forming the aryldimethylsulphine methyl sulphate,  $SRMe_2 \cdot O \cdot SO_3Me$ . The corresponding aryldiethylsulphine salts are formed in the same manner but less readily.

*Phenyldimethylsulphine platinichloride*,  $(C_8H_{11}S)_2PtCl_6$ , forms orange, yellow crystals, melts and decomposes at  $165-166^\circ$ , and is slightly soluble in water.

*$\alpha$ -Naphthyldimethylsulphine platinichloride*,  $(C_{12}H_{13}S)_2PtCl_6$ , is obtained as a sandy, crystalline, flesh-coloured precipitate, which melts and decomposes at  $174^\circ$ .  *$\beta$ -Naphthyldimethylsulphine platinichloride* forms a flesh-coloured, crystalline powder, and melts and decomposes at  $177^\circ$ .

G. Y.

**Preparation of Aminonaphthols.** FRANZ SACHS (D.R.-P. 173522. Compare this vol., i, 829).—The sulphonic group of a naphtholsulphonic acid may be replaced with great facility by an amino-group when the acid is heated with sodamide at high temperatures, especially in the absence of air, or in the presence of inert diluting materials such as naphthalene or quinoline.  $\beta$ -Naphthol-7-sulphonic acid furnished 2-amino- $\beta$ -naphthol, whilst  $\alpha$ -naphthol-5-sulphonic acid gave rise to 5-amino- $\alpha$ -naphthol. These products were characterised by their dibenzoyl derivatives.

In some cases isomeric change occurred; thus  $\beta$ -naphthol-6-sulphonic



acid gave a good yield of 5-*amino-β*-naphthol and *β*-naphthol-8-sulphonic acid furnished a mixture of 5-*amino-β*-naphthol and other isomerides.

G. T. M.

**Resolution of Aminobenzyl-*β*-naphthol into its Optical Antipodes.** MARIO BETTI (*Gazzetta*, 1906, 36, ii, 392—394. Compare Abstr., 1901, i, 611).—Racemic aminobenzyl-*β*-naphthol (aminobenzylidene-*β*-naphthol) can be readily separated into its constituents by adding an alcoholic solution of tartaric acid to a solution of the compound in 95 per cent. alcohol; in the course of twelve hours, the liquid deposits the *d-amine-d-tartrate* in almost theoretical amount. This tartrate forms small, shining crystals and begins to soften and turn yellow at about 180° and decomposes above 240°.

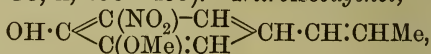
*d-Aminobenzyl-β-naphthol*,  $\text{NH}_2 \cdot \text{CHPh} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , crystallises from ether in white, silky needles, melts at 137°, and in benzene solution has  $[\alpha]_D + 58.84^\circ$  at 18°. Its *hydrochloride* has  $[\alpha]_D + 52.89^\circ$  in alcoholic solution at 18°.

*l-Aminobenzyl-β-naphthol* melts at 136—137°, and has  $[\alpha]_D - 58.96^\circ$ . Its *hydrochloride* has  $[\alpha]_D - 52.51^\circ$ .

It is noteworthy that the racemic compound melts at a lower temperature (124°) than its constituent isomerides, this being very seldom the case.

T. H. P.

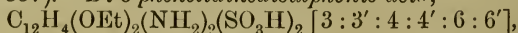
**Nitroisoeugenol.** ERNESTO PUXEDDU and MATTEO COMELLA (*Gazzetta*, 1906, 36, ii, 450—455).—*Nitroisoeugenol*,



prepared by the action of nitric acid on *isoeugenol* in acetic acid solution, separates from amyl or *isobutyl* alcohol in a reddish-yellow, amorphous mass decomposing at about 150°, and is readily soluble in alcohol or chloroform; it dissolves in concentrated nitric acid, giving a reddish-brown coloration, and in concentrated sulphuric acid forming an intensely brown solution; it is very readily soluble in dilute alkali solution, yielding a blood-red liquid with a peculiar odour. Its *bromo-derivative*,  $\text{C}_7\text{H}_7\text{O}_4\text{N} \cdot \text{CBr} \cdot \text{CHMe}$  or  $\text{C}_7\text{H}_7\text{O}_4\text{N} \cdot \text{CH} \cdot \text{CBr} \cdot \text{Me}$ , separates from alcohol as a reddish-yellow, amorphous powder, and begins to decompose at 175°; it dissolves in amyl alcohol, acetic acid, concentrated nitric or sulphuric acid or dilute alkali solution, and, to a slight extent, in ether or light petroleum. Its *acetyl* derivative,  $\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}$ , is deposited from alcohol as a yellowish-brown, amorphous powder decomposing above 200°.

T. H. P.

**Preparation of a Di-*o*-phenetidinedisulphonic Acid.** AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 174497. Compare this vol., i, 837).—*Di-o-phenetidinedisulphonic acid*,



is readily produced by treating di-*o*-phenetidine with fuming sulphuric acid at moderately low temperatures; it is readily soluble in water, whereas its sodium salt dissolves only sparingly and crystallises from water in lustrous leaflets.

G. T. M.

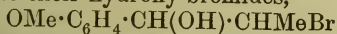
**Preparation of 4-Alkyloxy- $\alpha$ -naphthols.** BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 173730).—Generally the two hydroxyl groups of the dihydroxynaphthalenes are alkylated with equal readiness, so that the dialkyloxynaphthalenes are produced, but it now found that 1 : 4-dihydroxynaphthalene readily undergoes monoalkylation when the etherification process is discontinued so soon as the dihydroxy-compound has disappeared.

4-Methoxy- $\alpha$ -naphthol,  $\text{OMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , is prepared by dissolving 1 : 4-dihydroxynaphthalene in cold methyl-alcoholic hydrochloric acid and leaving the solution at the ordinary temperature for fifteen hours. When crystallised from light petroleum or benzene, the ether separates in colourless needles and melts at  $131^\circ$  (Abstr., 1900, i, 601).

4-Ethoxy- $\alpha$ -naphthol, produced by heating 1 : 4-dihydroxynaphthalene with alcoholic hydrochloric acid for thirty minutes, crystallises in colourless needles and melts at  $104\text{--}105^\circ$  (*loc. cit.*).

4-isoAmyloxy- $\alpha$ -naphthol forms colourless needles and melts at  $98^\circ$ .  
G. T. M.

**Preparation of Anethole and isoSafrole Oxides.** PAUL HÖRING (D.R.-P. 174496).—The dibromides of anethole and isosafrole when warmed with granulated marble in moist acetone solution are readily converted into their hydroxy-bromides,



and  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CHMeBr}$ . These substances or their acetyl derivatives when warmed with alcoholic sodium hydroxide or ethoxide lose another molecule of hydrogen bromide and become transformed into the corresponding oxides.

Anethole oxide,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{CHMe} \\ \diagup \\ \text{O} \end{smallmatrix}$ , is an oil boiling at  $132^\circ$  under 11 mm. pressure and having a sp. gr. 1.0637 at  $17^\circ$ . When warmed at  $190\text{--}210^\circ$  under ordinary pressure, the oxide undergoes isomeric change into the ketone,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{COMe}$ , which boils at  $267\text{--}269^\circ$  under ordinary pressure and at  $136\text{--}138^\circ$  under 12 mm. pressure and has a sp. gr. 1.0707 at  $17^\circ$ .

isoSafrole oxide,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \begin{smallmatrix} \text{CHMe} \\ \diagup \\ \text{O} \end{smallmatrix}$ , is a colourless oil having a more pleasant odour than the preceding oxide; it boils at  $149\text{--}151^\circ$  under 12 mm. pressure and has a sp. gr. 1.2128 at  $17^\circ$ . At  $200\text{--}220^\circ$  this oxide is transformed with development of heat into the isomeric ketone,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{COMe}$ ; this boils at  $149\text{--}151^\circ$  under 11 mm. or at  $283\text{--}284^\circ$  under the ordinary pressure, and has the sp. gr. 1.2017 at  $17^\circ$ .  
G. T. M.

**Amount of Cholesterol in Fats and Mineral Oils and their Probable Genetic Relationships.** M. A. RAKUSIN (*Chem. Zeit.*, 1906, 30, 1041—1042).—The presence of cholesterol in a number of oils of animal, vegetable, and mineral origin has been shown both by means of the colour reactions described by Tschugaeff, which consist in heating the substance with acetyl chloride in the presence of zinc chloride or with trichloroacetic acid, and by measurement of the optical rotation. The presence of cholesterol in mineral oils is

regarded as a clear proof of their origin from animal and vegetable sources; the low optical activity of some of the American oils is attributed to their containing the racemic modification of cholesterol.

P. H.

**Colour Phenomena Connected with Liquid Crystals.** [Cholesterol Compounds]. OTTO LEHMANN (*Chem. Centr.*, 1906, ii, 858; from *Physikal. Zeit.*, 7, 578—584).—An account of the play of colours observed when cholesteryl acetate propionate, isobutyrate, *n*-valerate, isovalerate, decoate, or octoate are examined between crossed nicols. When fused cholesteryl decoate is slowly cooled, it passes through two modifications of liquid crystals. In the first form the crystals are very small and mobile, and exhibit feeble double refraction; in the second form the crystals are larger and less mobile, but their double refraction is greater. The colour phenomena exhibited by mixtures of the decoate or the benzoate with *p*-azoxyphenetole are also described.

P. H.

**Solubility of Certain Benzoates in Water: Strontium Benzoate.** RAFFAELLO PAJETTA (*Gazzetta*, 1906, 36, iii, 67—70).—The solubility of strontium benzoate is as follows in grams of anhydrous salt per 100 grams of solution: at 15·7°, 5·31; at 24·7°, 5·40; at 31·4°, 5·40; at 40·9°, 5·77. Of potassium benzoate (expressed similarly) at 17·5°, 41·1; at 25·0°, 42·4; at 33·3°, 44·0; at 50·0°, 46·6. Of normal lead benzoate, at 18°, 0·149; at 40·6°, 0·249; at 49·5°, 0·310. The solubility of zinc benzoate diminishes with rise of temperature: at 15·9°, 2·55; at 17·0°, 2·49; at 27·8°, 2·14; at 31·3°, 2·05; at 37·5°, 1·87; at 49·8°, 1·62; at 58·0°, 1·45.

W. A. D.

**Preparation of Benzoylalkylaminoethanols** [Alkylaminoethyl Benzoates]. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHIERING (D.R.-P. 175080).—By benzoylating the alkylaminoethanols or their salts, benzoyl derivatives are obtained which have valuable anæsthetic properties.

*Diethylaminoethyl benzoate*,  $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$ , obtained by treating diethylaminoethanol with benzoic anhydride in aqueous solution is a viscid oil; its hydrochloride separates from a mixture of alcohol and ether in long needles melting at 124—125°. This salt is much more soluble in water than the hydrochlorides of the known synthetical local anæsthetics: "holocaine," "eucaine," &c., and is much less toxic than "stovaine" (dimethylaminodimethylethylcarbinyl benzoate hydrochloride).

*Dimethylaminoethyl benzoate*,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$ , is a viscid oil; its hydrochloride readily dissolves in water or alcohol, but not in ether, crystallises in white leaflets, and melts at 136—137°.

*Methylaminoethyl benzoate* is an oil which forms a hydrochloride, crystallising in lustrous leaflets and melting at 108—109°.

*Diisoomylaminoethyl benzoate* crystallises from a mixture of ethyl acetate and light petroleum and melts at 87—88°; its oxalate crystallises from water in spherical aggregates of sparingly soluble needles and melts at 152—153°.

G. T. M.



**Reversible Reactions among Derivatives of Organic Acids.** JOACHIM BIEHRINGER and WILHELM BORSUM (*Ber.*, 1906, 39, 3348—3356).—The qualitative conditions are discussed under which a number of simple organic reactions become reversible. Thus, in sealed tubes at 150°, benzoic acid and acetyl chloride form benzoyl chloride and acetic acid, but at 120°, under ordinary pressure, change proceeds in the contrary direction. Whereas the interaction of benzoic acid and acetamide takes place in one direction only, ethyl acetate and benzamide yield acetamide and ethyl benzoate when heated for six hours under pressure at 260°, whilst the reverse change takes place on heating under pressure from 270° to 290°. Phenyl benzoate and ammonia interact in sealed tubes at 150°, whilst benzamide and phenol yield phenyl benzoate when heated. Other cases considered are the interaction of oxalic acid and acetamide, of benzoic acid and acetanilide, and of acetanilide and benzoyl chloride. Diacetyl-*o*-tolidine and *o*-tolidine when heated together in sealed tubes at 240° give rise to *monoacetyl-o-tolidine*, forming pale yellow crystals which melt at 133—135°, rapidly become green when exposed to the atmosphere, and decompose when moist at 100°.

E. F. A.

**Formation and Behaviour of Thiobenzanilide.** ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 379—384).—The author has prepared thiobenzanilide by the action of phosphorus pentasulphide on benzophenoneoxime and, after crystallising from alcohol and light petroleum, dissolving in dilute potassium hydroxide solution and precipitating by means of carbon dioxide and again crystallising from light petroleum, it melted at 96°. When dissolved in potassium hydroxide solution and boiled with silver nitrate, it is converted into benzanilide.

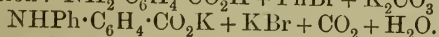
With silver nitrate, thiobenzanilide forms a salt,  $(C_{13}H_{11}NS)_2 \cdot AgNO_3$ , which separates in long, yellow needles, deflagrates and melts at 115°, and is soluble in chloroform, ethyl acetate, or methyl alcohol.

When reduced by means of zinc dust and potassium hydroxide solution, thiobenzanilide gives a yellow oil, which yields benzaldehyde on boiling with hydrochloric acid. As the thioanilides are easily obtained, this reaction affords a ready means of passing from an acid to the corresponding aldehyde.

T. H. P.

**Preparation of Arylanthranilic Acids.** IRMA GOLDBERG and FRITZ ULLMANN (D.R.-P. 173523).—Arylanthranilic acids are obtained when anthranilic acid is treated with aromatic bromo-derivatives in the presence of copper as a catalyst.

Phenylanthranilic acid is produced in a state of purity by heating to boiling a mixture of anthranilic acid, potassium carbonate, bromobenzene, and amyl alcohol to which a small amount of cuprous chloride has been added. The reaction takes place in accordance with the following equation:  $NH_2 \cdot C_6H_4 \cdot CO_2H + PhBr + K_2CO_3 =$



By replacing bromobenzene by other brominated benzene derivatives, similar arylanthranilic acids are prepared; *p*-bromonitrobenzene gives rise to 4-nitrophenylanthranilic acid,  $NO_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot CO_2H$ , which

crystallises in yellow needles and melts at  $211^{\circ}$ . The use of *p*-dibromobenzene leads to the formation of *p*-phenylenebis-*o*-aminobenzoic acid,  $C_6H_4(NH \cdot C_6H_4 \cdot CO_2H)_2$ , which melts at  $288^{\circ}$ ; it is very sparingly soluble in the ordinary organic media, but dissolves in boiling nitrobenzene. G. T. M.

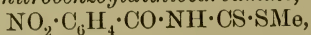
**Thiocyanates and Thiocarbimides. VI. TREAT B. JOHNSON** (*J. Amer. Chem. Soc.*, 1906, 28, 1454—1461. Compare Wheeler and Johnson, *Abstr.*, 1902, i, 760).—Phenylthioacetic, *m*- and *p*-bromothiobenzoic, and *m*-nitrothiobenzoic acids have been prepared by dissolving the corresponding acyl chlorides in a solution of potassium hydrogen sulphide and treating the resulting potassium salts with hydrochloric or sulphuric acid. These thiol acids react smoothly with methyl, ethyl, and benzyl thiocyanates with formation of the corresponding dithiocarbamates. Phenylthioacetic, *p*-bromothiobenzoic, and *m*-nitrothiobenzoic acids react quantitatively with phenylthiocarbimide with production of the corresponding acylanilines.

[With ERNEST BATEMAN, ERIK S. PALMER, and CHARLES A. BRAUTLECHT.]—*Phenylthioacetic acid*,  $CH_2Ph \cdot CO \cdot SH$ , is obtained as a limpid oil, and when left in the air is slowly converted into the disulphide. *Diphenylacetyl disulphide*,  $(CH_2Ph \cdot CO)_2S_2$ , prepared by suspending finely powdered iodine in an aqueous solution of sodium phenylthioacetate, crystallises from alcohol in transparent plates and melts at  $62^{\circ}$ . *Methyl phenylacetyldithiocarbamate*,  $CH_2Ph \cdot CO \cdot NH \cdot CS \cdot SMe$ , crystallises in slender prisms and melts at  $133^{\circ}$ . The corresponding *ethyl* ester separates from alcohol in lemon-yellow prisms and melts at  $125^{\circ}$ .

*m*-Bromothiobenzoic acid,  $C_6H_4Br \cdot CO \cdot SH$ , separates from light petroleum as a pale yellow, crystalline powder, melts at  $58^{\circ}$ , and is very soluble in alcohol, ether, or benzene. *Methyl m*-bromobenzoyldithiocarbamate,  $C_6H_4Br \cdot CO \cdot NH \cdot CS \cdot SMe$ , crystallises in needles and melts at  $124^{\circ}$ ; the corresponding *ethyl* and *benzyl* esters crystallise in prisms and melt at  $131^{\circ}$  and  $113^{\circ}$  respectively.

*p*-Bromothiobenzoic acid,  $C_6H_4Br \cdot CO \cdot SH$ , crystallises from hot alcohol in prisms and melts at  $78$ — $79^{\circ}$ . *p*-Bromobenzoylaniline melts at  $201$ — $202^{\circ}$  instead of at  $197^{\circ}$  as stated by Raveill (*Abstr.*, 1884, 600). *Methyl p*-bromobenzoyldithiocarbamate,  $C_6H_4Br \cdot CO \cdot NH \cdot CS \cdot SMe$ , crystallises in needles and melts at  $152^{\circ}$ ; the corresponding *ethyl* ester forms pale yellow needles and melts at  $116^{\circ}$ .

*m*-Nitrothiobenzoic acid,  $NO_2 \cdot C_6H_4 \cdot CO \cdot SH$ , forms light yellow, prismatic crystals and melts at  $89$ — $90^{\circ}$ ; the *sodium* salt is very soluble in water. *Methyl m*-nitrobenzoyldithiocarbamate,



crystallises from benzene in yellow needles, melts at  $162^{\circ}$ , and is very soluble in benzene and sparingly so in alcohol; the corresponding *ethyl* ester separates from hot alcohol in yellow prisms and melts at  $158^{\circ}$ . E. G.

**Unsaturated Compounds. II. The Addition of Free Hydroxylamine to Cinnamic Acid. Constitution and Derivatives of  $\beta$ -Hydroxylamino- $\beta$ -phenylpropionic Acid.** THEODOR POSNER (*Ber.*, 1906, 39, 3515—3529. Compare *Abstr.*, 1904, i, 160). —The substance produced by the direct addition of hydroxylamine to cinnamic acid was formerly regarded as being  $\alpha$ -hydroxylamino- $\beta$ -phenylpropionic acid, because on reduction it yielded the compound which was then considered to be  $\alpha$ -aminodihydrocinnamic acid. The latter has since been shown to be  $\beta$ -amino- $\beta$ -dihydrocinnamic acid (*Abstr.*, 1905, i, 577), and consequently the original additive compound is  $\beta$ -hydroxylamino- $\beta$ -phenylpropionic acid,  $\text{OH}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , melting at  $166^\circ$ . *Diacetyl* and *dibenzoyl- $\beta$ -hydroxylamino- $\beta$ -phenylpropionic acids* form colourless crystals melting respectively at  $166$ — $167^\circ$  and  $110^\circ$ .

On oxidation with ammoniacal silver nitrate, the hydroxylamino-acid furnishes 3-phenylisooxazolone, the *nitroso*-derivative of which melts at  $143^\circ$ .

*Acetyl-3-phenylisooxazolone*,  $\text{NAc} \begin{smallmatrix} \text{CPh}\cdot\text{CH} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{smallmatrix}$ , forms white needles melting at  $137$ — $138^\circ$ ; it is readily soluble in aqueous ammonia and alkalis, and is reprecipitated by dilute acids.

*Bromo-3-phenylisooxazolone*,  $\text{C}_9\text{H}_6\text{O}_2\text{NBr}$ , produced by brominating 3-phenylisooxazolone in chloroform solution, separates from methyl alcohol in prismatic crystals and melts at  $121$ — $122^\circ$ .  $\beta$ -Hydroxylamino- $\beta$ -phenylpropionic acid is very readily alkylated by treatment with a mixture of the appropriate alcohol and concentrated hydrochloric acid on the water-bath.  *$\beta$ -Methoxylamino- $\beta$ -phenylpropionic acid* and the *ethoxyl* compound crystallise in colourless needles and melt respectively at  $101\cdot5$ — $102\cdot5^\circ$  and  $74\cdot5$ — $75^\circ$ . Both alkyl derivatives are readily hydrolysed by alkalis, although fairly stable to cold dilute acids. They both furnish, on oxidation with ammoniacal silver nitrate, good yields of 3-phenylisooxazolone.

,  *$\beta$ -Nitrosohydroxylamino- $\beta$ -phenylpropionic acid*,  $\text{CHPh}\cdot\text{N}(\text{OH})(\text{NO})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is a very unstable compound obtained by the action of nitrous acid on  $\beta$ -hydroxylamino- $\beta$ -phenylpropionic acid or its alkyl derivatives; when quickly prepared and isolated, it forms a colourless, crystalline powder melting at  $133^\circ$ . On heating or even on dissolving it in warm benzene, it evolves nitrous fumes and changes into *2-hydroxy-3-phenylisooxazolidone*,  $\text{OH}\cdot\text{N} \begin{smallmatrix} \text{CHPh}\cdot\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{smallmatrix}$ , a pale yellow, crystalline powder easily soluble in methyl or ethyl alcohol, and dissolving readily in aqueous alkalis, but not in dilute acids.

*2-Methoxy-3-phenylisooxazolidone*,  $\text{OMe}\cdot\text{N} \begin{smallmatrix} \text{CHPh}\cdot\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{smallmatrix}$ , is obtained either by the action of methyl sulphate on the foregoing compound, or by the decomposition in benzene solution of the nitroso-compound of  $\beta$ -methoxylamino- $\beta$ -phenylpropionic acid; it crystallises from benzene in rectangular prisms and melts at  $128^\circ$ .

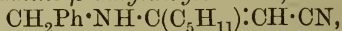


2-Ethoxy-3-phenylisooxazolidone melts at 109°, and, like the foregoing methyl compound, is insoluble in aqueous alkalis.

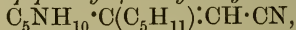
On attempting to acetylate 2-hydroxy-3-phenylisooxazolidone with acetic anhydride, a crystalline product was obtained which was decomposed by sodium carbonate into an acidic and a neutral part. The acidic compound has a composition approximating to  $C_{18}H_{14}O_6$ , the neutral substance corresponds with the formula  $C_{22}H_{18}O_4$ . G. T. M.

**Condensation of Acetylenic Nitriles with Amines. General Method of Synthesis of  $\beta$ -Substituted Derivatives of  $\beta$ -Amino-substituted Acrylonitriles.** CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 143, 553—555. Compare this vol., i, 148, 240, 276, 432).—Phenylpropionitrile unites directly with piperidine to form  $\beta$ -piperidyl- $\beta$ -phenylacrylonitrile,  $C_5NH_{10} \cdot CPh \cdot CH \cdot CN$ , which is a neutral substance melting at 92°, stable towards alkalis, but readily hydrolysed by hydrochloric, picric, or oxalic acid with the regeneration of piperidine and formation of cyanoacetophenone, according to the equations:  $C_5NH_{10} \cdot CPh \cdot CH \cdot CN + H_2O = C_5NH_{11} + [OH \cdot CPh \cdot CH \cdot CN] \rightarrow CPh \cdot CH_2 \cdot CN$ .

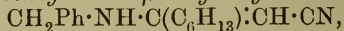
This reaction between acetylenic nitriles and primary or secondary amines is a general one, and the following compounds were thus prepared:  $\beta$ -Benzylamino- $\beta$ -amylacrylonitrile,



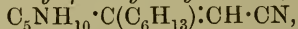
melting at 64—65°;  $\beta$ -piperidyl- $\beta$ -amylacrylonitrile,



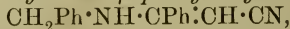
boiling at 218—219° (corr.) under 23 mm. pressure, and having a sp. gr. 0.950 at 24°;  $\beta$ -benzylamino- $\beta$ -hexylacrylonitrile,



melting at 48°;  $\beta$ -piperidyl- $\beta$ -hexylacrylonitrile,



boiling at 236—238° (corr.) under 27 mm. pressure and having a sp. gr. 0.943 at 24°;  $\beta$ -benzylamino- $\beta$ -phenylacrylonitrile,

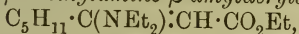


melting at 86°;  $\beta$ -diethylamino- $\beta$ -phenylacrylonitrile,  $NEt_2 \cdot CPh \cdot CH \cdot CN$ , melting at 70°; and  $\beta$ -piperidyl- $\beta$ -phenylacrylonitrile, melting at 92°.

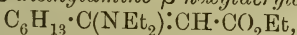
M. A. W.

**Condensation Products of Acetylenic Esters and Amines.** CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, 143, 596—598. Compare preceding abstract).—The acetylenic esters readily condense with primary and secondary amines to form the amino-substituted derivative of the corresponding ethylene ester, and these compounds do not form salts with acids as stated by Ruhemann and Cunningham (*Trans.*, 1899, 75, 954), but are hydrolysed with regeneration of the base and formation of the corresponding  $\beta$ -ketonic ester. Thus, ethyl phenylpropionate condenses with diethylamine to form ethyl  $\beta$ -diethylamino- $\beta$ -phenylacrylate,  $NEt_2 \cdot CPh \cdot CH \cdot CO_2Et$ , which is readily hydrolysed in the cold by acids yielding the corresponding salt of diethylamine and ethyl benzoylacetate. The hydrolysis is effected by passing hydrogen chloride into an ethereal solution of the compound or by adding to the solution an equivalent quantity of picric or

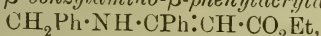
oxalic acid dissolved in ether and alcohol. The following compounds were obtained: *ethyl β-diethylamino-β-amylacrylate*,



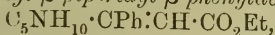
boiling at 170—178° under 26 mm. pressure and having a sp. gr. 0.9316 at 24°; *ethyl β-diethylamino-β-hexylacrylate*,



boiling at 185—195° under 24 mm. pressure, and having a sp. gr. 0.9211 at 24°; *ethyl β-benzylamino-β-phenylacrylate*,



melting at 72°; and *ethyl β-piperidyl-β-phenylacrylate*,



boiling at 225—228° (corr.) under 23 mm. pressure, and having a sp. gr. 1.072 at 24°.

M. A. W.

**Preparation of Hydroxyethyl Salicylate.** BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 173776).—*β-Hydroxyethyl salicylate*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , the hitherto unknown monosalicylate of ethylene glycol, is readily prepared by the interaction of the metallic salicylates and the ethylene halogen hydrins; thus on heating at 140—150° for several hours a mixture of sodium salicylate and ethylene chlorohydrin, and extracting the product successively with water and ether, the ester is obtained as solid melting at 37°, and boiling at 169—170° under 12 mm. pressure. With ferric chloride it develops a violet coloration.

G. T. M.

**Reductions with Phenylhydrazine. I. New Method of Preparing 5-Aminosalicylic Acid.** ERNESTO PUXEDDU (*Gazzetta*, 1906, 36, ii, 87—89. Compare Abstr., 1905, i, 842).—5-Aminosalicylic acid,  $[\text{CO}_2\text{H}:\text{OH}:\text{NH}_2=1:2:5]$ , is easily prepared by warming 5-nitrosalicylic acid with phenylhydrazine; action begins at slightly above 100° and proceeds rapidly. The yield is good.

W. A. D.

**Constitution of the Aromatic Purpuric Acids. IX. Behaviour on Oxidation with Potassium Hypobromite.** WALTHER BORSCHKE and G. GAHRTZ (*Ber.*, 1906, 39, 3359—3366. Compare Abstr., 1905, i, 894).—Potassium *m*-purpurate when oxidised with potassium hypobromite yields 2:6-dinitro-3-hydroxybenzonitrile of which the *aniline* derivative crystallises in golden-yellow needles melting at 162—163°, and the *acetate* forms yellow, glistening platelets melting at 122—123°. Potassium *o*-tolylpurpurate under similar treatment yields 2:6-dinitro-3-hydroxy-4-toluonitrile. 4-Bromo-2:6-dinitro-3-hydroxybenzonitrile, obtained on oxidising potassium bromo-*m*-purpurate, crystallises in yellow needles melting at 152°, the *aniline* salt forms canary-yellow needles melting at 185°, whilst 4-bromo-2:6-dinitro-3-hydroxybenzamide separates from water in glistening, yellowish-white plates melting at 231°. Potassium naphthylpurpurate gives rise to 2:4-dinitro-1-hydroxy-3-naphthonitrile, crystallising in bright yellow, glistening needles which melt at 165—166°: the *aniline* salt is a yellow, crystalline powder melting at 152°.

*Cyanopicric acid* (2:4:6-trinitro-3-hydroxybenzonitrile), prepared

by nitration of dinitrohydroxybenzonitrile, crystallises in yellowish-white needles or plates and melts at  $131-132^{\circ}$ : the *aniline* salt forms yellow needles which melt at  $179-180^{\circ}$ . E. F. A.

**Conversion of Racemic Compounds into Optically Active Compounds.** WILLY MARCKWALD and DAVID M. PAUL (*Ber.*, 1906, 39, 3654—3655. Compare Abstr., 1905, i, 285).—When *l*-mandelic acid is heated with an equivalent quantity of brucine for twenty hours at  $150-160^{\circ}$  and the acid recovered, it is found to be dextrorotatory with  $[\alpha]_D + 0.45^{\circ}$  to  $+ 0.6^{\circ}$ . When *r*-mandelic acid is heated with other alkaloids, the recovered acid is found to be dextrorotatory, but the amount of rotation varies with the alkaloid employed. With strychnine the recovered acid has  $[\alpha]_D + 2.05^{\circ}$  and with nicotine  $+ 0.4^{\circ}$ .

*r-p*-Methoxymandelic acid has  $[\alpha]_D + 1.2^{\circ}$  to  $+ 1.5^{\circ}$ , when heated with brucine or strychnine, and  $\beta$ -phenyllactic acid has  $[\alpha]_D - 0.16^{\circ}$  when heated with brucine for five hours at  $150-160^{\circ}$ .

$\alpha$ -Methylbutyric acid, and  $\beta$ -phenyl- $\alpha$ -methylpropionic acid are not affected when heated with strychnine, neither is  $\alpha$ -methoxyphenylacetic acid when heated with brucine, whereas with strychnine it has  $[\alpha]_D + 0.32^{\circ}$ . J. J. S.

**Di-*p*-methylbenzilic Acid (*pp'*-Tolilic Acid).** ERWIN GISIGER (*Ber.*, 1906, 39, 3589. Compare Gattermann, this vol., i, 589).—Di-*p*-methylbenzilic acid is prepared by boiling di-*p*-methylbenzoin with 20 per cent. potassium hydroxide solution through which a current of air is passed; it melts at  $135^{\circ}$  and gives a blood-red coloration with concentrated sulphuric acid. The *barium* salt,  $(C_{16}H_{15}O_3)_2Ba$ , forms white leaflets; the *methyl* ester,  $C_{17}H_{18}O_3$ , crystallises from alcohol in needles and melts at  $82^{\circ}$ ; the *acetyl* derivative,  $C_{18}H_{18}O_4$ , separates from light petroleum in small crystals, melts at  $92^{\circ}$ , and is readily hydrolysed. G. Y.

**Influence of the Position of the Ethylene Linking on the Electro-affinity and Characters of Unsaturated Alicyclic Acids.** GINO ABATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 220—226).—From a study of the affinity constants of the naphthoic and the hydronaphthoic acids, benzoic acid, phthalic and the hydrophthalic acids, it is seen that, apart from the strongly negative character of the aromatic nucleus, the presence and position of the double linking have no small influence on the energy of an acid. In the  $\alpha\alpha$ - and  $\beta\gamma$ -positions, the double linking produces a great increase in the value of the electrical conductivity, whilst when it is in the  $\alpha\beta$ - or  $\gamma\delta$ -position, the values of the conductivity are not much greater than those of the corresponding saturated acids.

The explanation given by Fichter and Pfister (Abstr., 1904, i, 965) of their results on the basis of Thiele's theory of partial valencies is fallacious. According to Thiele's theory, the  $\gamma\delta$ -, &c., acids should be as unsaturated as the  $\beta\gamma$ -acids, whilst the fact is that they are far weaker than these and have constants not differing greatly from those of the  $\alpha\beta$ -acids. This contradiction of Thiele's theory is confirmed by the constants for acids having a double linking in the  $\alpha\alpha$ -position with



respect to the two carboxyl groups. For instance, in the case of the four tetrahydrophthalic acids, the  $\Delta^1$ -acid should, according to Thiele's theory, be the most saturated and should hence be the least energetic. Instead, however, the constant of this acid is the greatest of the four and is five times that of the  $\Delta^4$ -acid, which has six partial valencies. Similar disagreement with this theory is offered by the constants for citraconic, mesaconic, and itaconic acids.

When treated with alkali hydroxides, unsaturated  $\beta\gamma$ -acids do not pass completely into the  $\alpha\beta$ -isomerides, the reaction being reversible. Further, in the reduction of phthalic acid by means of sodium amalgam, there is a marked tendency to the formation of acids with a double linking in the  $\beta\gamma$ -position, although the temperature is kept at about  $150^\circ$  for some three hours and the proportion of sodium hydroxide present in the liquid ultimately reaches 15 or 20 per cent. It is therefore unsafe to assign the  $\beta\gamma$ -constitution to acids on the sole ground that they undergo transformation with alkali hydroxides, as has been done by Perkin and Pickles in the case of the tetrahydroisophthalic acids (Trans., 1905, 87, 293).

T. H. P.

**Hydrophthalic Acids: Affinity Constants of Two New Anhydrides.** II. GINO ABATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 207—210. Compare Abstr., 1905, i, 599).—Conductivity measurements of solutions of the two new hydrophthalic anhydrides (*loc. cit.*) lead to the following values: (1) For  $\Delta^{1:3}$ -dihydrophthalic anhydride,  $\mu_\infty = 377$  and  $K = 0.0798$ . (2) For *cis*- $\Delta^3$ -tetrahydrophthalic anhydride,  $\mu_\infty = 376$  and  $K = 0.0581$ .

Titration of aqueous solutions of the anhydrides with barium hydroxide solution, using methyl-orange as indicator, shows that, although they cannot be obtained in the solid state in the form of acids, they behave as acids when dissolved in water; this fact is also shown by the high value of the affinity constants, which are in accord with the constitutions given previously (*loc. cit.*), as it has been repeatedly observed that a double bond in the  $\beta\gamma$ -position effects a marked increase in the energy of unsaturated acids.

T. H. P.

**Hydrophthalic Acids: Transformation by Heat of the New Dihydrophthalic Anhydrides. Characters of the *p*-Methoxyphenylhydrophthalimides.** III. GINO ABATI and ANDREA CONTALDI (*Rend. Accad. Sci. Fis. Mat., Napoli*, 1906, [iii], 12, 211—219. Compare preceding abstract).—When heated at about  $225^\circ$  for some two hours,  $\Delta^{1:3}$ -dihydrophthalic anhydride (compare Abati and de Bernardinis, Abstr., 1905, i, 599) is converted into another anhydride, which is possibly the  $\Delta^{2:5}$ -compound regarded by von Baeyer (Abstr., 1892, 1211) as incapable of existence. When its alcoholic solution is treated with *p*-anisidine, it yields *p*-methoxyphenyl-dihydrophthalimide, which forms white needles melting at  $98^\circ$ , and as it does not correspond with any of the derivatives obtained from the known dihydrophthalic anhydrides, must be regarded as the  $\Delta^{2:5}$ -compound. Hence, when the  $\Delta^{1:3}$ -anhydride is heated, the double linking in the  $\alpha\alpha$ -position migrates to the neighbouring  $\alpha\beta$ -position, whilst the other double linking retains its place in the  $\beta\gamma$ -position.

*p*-Methoxyphenyl- $\Delta^{1:3}$ -dihydrophthalimide forms yellow crystals melting at  $104^\circ$ .

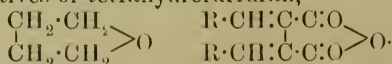
A table is given showing the melting points of the dihydrophthalic and tetrahydrophthalic anhydrides, and the melting points and colours of the *p*-methoxyphenylimides formed from these anhydrides. In general, the anhydrides exhibiting similar physical and chemical characters yield imides similar to one another.

Halochromism is exhibited by all the dihydrophthalimides when dissolved in sulphuric acid, whilst of the tetrahydrophthalimides only the  $\Delta^1$ - and  $\Delta^3$ -compounds show this phenomenon, a fact which illustrates the influence of the position of the ethylene linking with respect to the phenyldiketopyrrolidine grouping. T. H. P.

**$\beta$ -Benzylideneglutaric Acid.** HERMANN A. MÜLLER (*Ber.*, 1906, 39, 3590—3591. Compare Fittig and Roedel, *Abstr.*, 1895, i, 141; Fittig, *Abstr.*, 1898, i, 11; Fichter and Bauer, *Abstr.*, *ibid.*, 662; Thiele and Meisenheimer, *Abstr.*, 1899, i, 603).—The condensation of benzaldehyde with ethyl tricarballoylate in ethereal solution in presence of sodium ethoxide leads to the formation of  $\beta$ -benzylideneglutaric anhydride,  $\text{CHPh}\cdot\text{C}\begin{matrix} \diagup \text{CH}_2\cdot\text{CO} \\ \diagdown \text{CH}_2\cdot\text{CO} \end{matrix}\text{O}$ , which crystallises in colourless, strongly refracting leaflets or long, flat prisms, melts at  $44\text{--}45^\circ$ , is volatile in a current of steam, and with alkali hydroxides forms salts of  $\beta$ -benzylideneglutaric acid; the acid is unstable and yields the anhydride immediately on liberation.  $\beta$ -Benzylideneglutaranil,  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ , formed by heating the anhydride with aniline, crystallises in glistening leaflets and melts at  $90^\circ$ . When boiled with aqueous sodium hydroxide,  $\beta$ -benzylideneglutaric acid yields two acids, melting at  $184^\circ$  and  $145^\circ$  respectively. G. Y.

**Colour of Fulgides and of other Unsaturated Compounds.** HANS STOBEE (*Annalen*, 1906, 349, 333—371).—The author cites numerous examples to show that the colour of the fulgenic acids and of similarly constituted substances is to be explained not only by the number and the position of the chromophoric phenyl and carboxyl groups in the carbon chain, but also by the influence of the conjugated double linkings. The fact that  $\alpha$ : $\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -butadiene- $\delta$ -carboxylic acid and  $\alpha$ : $\delta$ -diphenylfulgenic acid are colourless, whereas  $\alpha$ : $\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -butadiene- $\gamma$ -carboxylic acid is yellow, is accounted for on stereochemical grounds.

The more pronounced colour of the fulgides is not due to heterocyclic ring formation; examples are quoted to show that such formation results in a diminution or disappearance of the colour. The selective absorption of the fulgides can be brought into harmony with the "quinone" theory, inasmuch as these compounds are ortho- and para-quinonoid derivatives of tetrahydrofurfuran,



In chemical and physical properties they resemble Thiele's fulvenes (*Abstr.*, 1900, i, 298) and "quinonoid" hydrocarbons (*Abstr.*, 1904, i, 491).

The absorption spectra of certain fulgides have been measured in *N*/32 chloroform solution.

Tetramethylfulgide absorbs only in the ultra-violet; the presence of each phenyl group increases by  $58\mu$ , the length of the absorption band in the visible spectrum.

C. S.

**Condensation Products of Gallic Acid with Formaldehyde and Carbamide, or with Formaldehyde and Urethanes.** ARNOLD VOSWINKEL (D.R.-P. 171788).—Carbamide (1 mol.) condenses with gallic acid (2 mols.) and formaldehyde, giving rise to a methylene-carbamido-gallic acid having the composition  $C_{17}H_{16}O_{11}N_2$ . The condensation occurs in dilute alcohol in the presence of mineral acids, and the product is a pale grey powder which melts and decomposes at  $210^\circ$  and has an intensely bitter taste. The compound forms an insoluble basic bismuth salt.

G. T. M.

**Cetraric Acid.** OSCAR SIMON (*Arch. Pharm.*, 1906, 244, 459—466. Compare Abstr., 1903, i, 98).—The products obtained by treating cetraric acid with aqueous sodium hydroxide and zinc powder have been examined further. From the crude mixture of phenols, 3:5-dihydroxy-1:2-dimethylbenzene,  $C_8H_{10}O_2$  (Abstr., 1904, i, 406), has been isolated. When treated with bromine (4 mols.) in chloroform solution, it yields crystalline *dibromo-* and *tribromo-*derivatives; these melt at  $98$  and  $112^\circ$  respectively, and are converted into the ketobromide,  $C_8H_6O_2Br_4$ , when treated with excess of bromine in acetic acid solution.

From the same source yellow crystals were obtained which melt at  $119$ — $121^\circ$ , contain C 63.4, H 5.5, and have molecular weight 164 (determined cryoscopically in naphthalene); this *substance* does not contain methoxyl; it is soluble in alkali hydroxides and carbonates and gives a green coloration with ferric chloride; when it is treated in the cold with aniline in alcoholic solution, it yields an orange-yellow *anilide*, which melts and decomposes at  $189$ — $190^\circ$ , and contains C 73.4, H 6.1, N 7.0; and with excess of bromine in acetic acid solution it forms a *bromide* which melts at  $116$ — $121^\circ$ , contains C 17.5, H 1.8, Br 76.6, and is insoluble in aqueous sodium carbonate.

From the resinous mass obtained when the product of the action of aqueous sodium hydroxide and zinc powder is poured into dilute sulphuric acid, a yellow, crystalline *substance* has been obtained which melts at  $129$ — $132^\circ$ , contains C 65.5, H 6.1 ( $C_{10}H_{12}O_3$ ?), and has molecular weight 180 (determined cryoscopically in naphthalene); this substance, when treated in alcoholic solution with aniline, forms a red *anilide*,  $C_{16}H_{17}O_2N$ , which melts and decomposes at  $184^\circ$ , and when treated with a large excess of bromine in acetic acid solution, it yields the ketobromide,  $C_8H_6O_2Br_4$ .

When cetraric acid,  $C_{20}H_{18}O_9$ , is treated with bromine, either directly or in acetic acid or chloroform solution, it yields a *bromo-*derivative, probably a mixture of  $C_{20}H_{16}O_9Br_2$  and  $C_{19}H_{16}O_7Br_2$ , which melts at  $181$ — $185^\circ$ , still contains methoxyl, and dissolves slowly in aqueous sodium carbonate.

C. F. B.

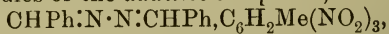


**Behaviour of Benzaldehyde in Presence of Iodoxybenzene and under the Action of Light.** LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 375—379).—The interaction of benzaldehyde and iodoxybenzene under the influence of light yields: (1) Benzoic acid, by the reaction,  $2\text{Ph}\cdot\text{CHO} + \text{PhIO}_2 = 2\text{Ph}\cdot\text{CO}_2\text{H} + \text{PhI}$ . (2) A *trimeric benzaldehyde*,  $(\text{C}_7\text{H}_6\text{O})_3$ , which separates from acetic acid in stable, white crystals melting at  $250^\circ$ . (3) Stilbene, which may be formed either by the reduction of benzaldehyde by iodosobenzene or formed as an intermediate product in the oxidation of benzaldehyde to benzoic acid by the iodoxybenzene:  $2\text{Ph}\cdot\text{CHO} + 2\text{Ph}\cdot\text{OI} = \text{CHPh}\cdot\text{CHPh} + 2\text{Ph}\cdot\text{IO}_2$ ; or by the decomposition of a complex oily product,  $\text{CHPh}\cdot\text{I}\cdot\text{Ph}$  or  $\text{Ph}\cdot\text{I}(\text{CHPh})_2$ , which could not be obtained pure, and yields stilbene and iodobenzene on distillation.

T. H. P.

**Additive Products Formed by Trinitrobenzene with Aromatic Substances containing the Side-chain  $\cdot\text{CH}\cdot\text{N}\cdot$ .** ROBERTO CIUSA (*Gazzetta*, 1906, 36, ii, 94—98).—Benzaldehydephenylhydrazone combines with trinitrobenzene in warm alcoholic solution to form the *additive* compound  $\text{CHPh}\cdot\text{N}_2\text{HPh}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3$ , which forms dark red crystals and melts at  $134^\circ$ ; the analogous *trinitrotoluene* derivative,  $\text{CHPh}\cdot\text{N}_2\text{HPh}\cdot\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ , forms dark red needles and melts at  $84^\circ$ . *Benzaldehydephenylhydrazone picrate*,  $\text{CHPh}\cdot\text{N}_2\text{HPh}\cdot\text{C}_7\text{H}_3\text{O}_7\text{N}_3$ , prepared similarly by using picric acid, forms blackish-violet needles with a metallic reflex, and melts at  $117^\circ$ . *m-Nitrobenzaldehydephenylhydrazone picrate*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}_2\text{HPh}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises in chestnut coloured needles with a violet sheen and melts at  $118^\circ$ .

Benzylideneazine combines with trinitrotoluene in alcoholic solution, giving yellow needles of the *additive* compound,



which melts at  $97$ — $98^\circ$ . *Benzylideneazine picrate*,  $\text{C}_{14}\text{H}_{12}\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , forms small, canary-yellow needles and melts at  $148^\circ$ . *Furfuralazine picrate*,  $(\text{C}_4\text{H}_3\text{O}\cdot\text{CH})_2\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises from alcohol in greenish-yellow needles, darkens at  $155^\circ$ , and melts and decomposes at  $157^\circ$ . *Benzylideneaniline picrate*,  $\text{CHPh}\cdot\text{NPh}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises in golden-yellow needles and melts at  $183^\circ$ . *Salicylideneaniline picrate*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , forms lustrous, yellow needles and melts at  $153$ — $154^\circ$ . *Cinnamylideneaniline*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises in orange-yellow needles or plates and melts at  $139^\circ$ .

W. A. D.

**Some Aromatic Aldehydes and Ketones.** KARL AUWERS (*Ber.*, 1906, 39, 3757—3764. Compare Auwers and Hessenland, *Abstr.*, 1905, i, 434).—*p*-Methylhydrocinnamaldehyde (von Miller and Rohde, *Abstr.*, 1890, 978) is a colourless oil which boils at  $220$ — $230^\circ$  under atmospheric pressure, has a sp. gr. 0.9928 at  $18.5^\circ/18.5^\circ$ , and forms a *semicarbazone*,  $\text{C}_{11}\text{H}_{15}\text{ON}_3$ , crystallising in long, flat, glistening needles and melting at  $170$ — $171^\circ$ . *p*-Ethylbenzoylmethyl chloride,  $\text{C}_6\text{H}_4\text{Et}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , prepared by Friedel and Craft's synthesis from ethylbenzene and chloroacetyl chloride, crystallises from light petroleum in white scales, melts at  $38$ — $39^\circ$ , boils at  $145$ — $148^\circ$  under 8 mm. pressure, and forms a *semicarbazone*,  $\text{C}_{11}\text{H}_{14}\text{ON}_3\text{Cl}$ , crystallising in

slender, white needles and melting at 153—154°. *p*-Ethylbenzoyl-methyl acetate,  $C_6H_4Et \cdot CO \cdot CH_2 \cdot OAc$ , prepared by boiling the chloride with potassium acetate and glacial acetic acid, crystallises in white prisms, melts at 61—62°, and when boiled with alcoholic sodium hydroxide yields the *carbinol*,  $C_6H_4Et \cdot CO \cdot CH_2 \cdot OH$ . This crystallises in yellow leaflets, melts at 67—68°, and has a sweet flavour; the *semicarbazone*,  $C_{11}H_{15}O_2N_3$ , crystallises in white scales and melts at 161°. *p*-Ethylphenylacetaldehyde,  $C_6H_4Et \cdot CH_2 \cdot CHO$ , prepared by reducing the ketonic alcohol with sodium amalgam in aqueous alcoholic carbonate solution through which a current of carbon dioxide is passed, and treatment of the resulting glycol with concentrated sulphuric acid, is obtained as an oil; this has an odour of cuminaldehyde, and forms a *semicarbazone*,  $C_{11}H_{15}ON_3$ , crystallising in slender, white needles and melting at 162—164°.

*p*-Methylbenzoylmethyl chloride melts at 57—58° (compare Kuncell, Abstr., 1897, i, 282; Collet, Abstr., 1898, i, 139; Ryan, *ibid.*, 649); the acetate melts at 85—86° (83—83·5°, Collet, 1898, i, 123). *p*-Methylbenzoylcarbinol,  $C_6H_4Me \cdot CO \cdot CH_2 \cdot OH$ , crystallises in light yellow prisms, melts at 89—89·5°, and forms a *semicarbazone*,  $C_{10}H_{13}O_2N_3$ , crystallising in white needles and melting at 165°. Reduction of the ketonic alcohol with sodium amalgam and treatment of the *product* with concentrated sulphuric acid leads to the formation of only a small amount of an *oil*, which has a characteristic odour of elderberries, and forms a *semicarbazone*,  $C_{10}H_{13}ON_3$ , melting at 208°. A small amount of the same semicarbazone, but melting at 212—213°, is obtained from the product formed on boiling *p*-methyl- $\beta\beta$ -dichloroethyl benzene with aqueous potassium hydroxide.

*a*-Chloro-*p*-methylhydratropic acid,  $C_6H_4Me \cdot CClMe \cdot CO_2H$ , prepared by the action of hydrogen cyanide on *p*-methylacetophenone (compare Janssen, Abstr., 1889, 596) and treatment of the product with concentrated hydrochloric acid at 130° (Spiegel, Abstr., 1881, 277), crystallises from carbon disulphide and melts at 116—118°.

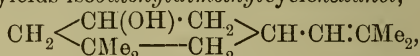
*p*-Methylhydratropaldehyde,  $C_6H_4Me \cdot CHMe \cdot COH$ , prepared by the action of ethyl chloroacetate and sodamide on *p*-methylacetophenone (compare Claisen, Abstr., 1905, i, 287), boils at 227—228° under atmospheric pressure, and is identical with the aldehyde obtained from cymene by Etard's reaction; it forms a semicarbazone crystallising in slender, white needles melting at 155—157°.

The supposed aldehyde-semicarbazone previously obtained (Abstr., 1905, i, 434) from dichloro-*p*-cuminic acid is now found to be the semicarbazone of *p*-tolylacetone; it is accompanied by a small amount of a *semicarbazone* of an aldehyde which remains in the mother liquors on recrystallisation.

5-Ethylsalicylaldehyde,  $OH \cdot C_6H_3Et \cdot COH$ , prepared from *p*-ethylphenol by Reimer's synthesis, is an oil; the *semicarbazone*,  $C_{10}H_{13}O_2N_3$ , crystallises in nacreous leaflets and melts at 208°. G. Y.

**Synthesis of a Ketone Isomeric with Xylitone.** EMIL KNOEVENAGEL and RUDOLF SCHWARTZ (*Ber.*, 1906, 39, 3441—3451. Compare Kerp and Müller, Abstr., 1898, i, 265; Pinner, Abstr., 1882, 941).—A compound isomeric with Pinner's xylitone may be

*See errata, V. 92, p. 1381*  
 synthesised by the action of sodium ethoxide on a mixture of ethyl acetoacetate and acetophenone; it is represented as isobutenyl-dimethylcyclohexenone,  $\text{CH}_2 \begin{smallmatrix} \text{CO} \text{---} \text{CH} \\ \text{CMe}_2 \text{---} \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{CMe}_2$ , and distils at 132—134° under 12 mm. pressure, or at 246° under atmospheric pressure. It is not readily volatile with steam, and has a sp. gr. 0.9365 at 19°/4°. The molecular refraction is higher even than what would be required for the enolic compound. It yields a tetrabromide, which is extremely unstable, a phenylhydrazone melting at 80—81°, an oxime,  $\text{C}_{12}\text{H}_{19}\text{ON}$ , melting at various temperatures between 85° and 108°, and a semicarbazone melting at 167—168°. When reduced with sodium and alcohol, it yields isobutenyldimethylcyclohexanol,



which boils at 122—123° under 12 mm. pressure, and has a sp. gr. 0.8886 at 23.5°/4° and  $n_D$  1.4675 at 23.5°. The dibromide is unstable, and the acetate distils at 244—247°. When oxidised with chromic acid mixture, the alcohol yields the corresponding ketone isobutenyldimethylcyclohexanone,  $\text{C}_{12}\text{H}_{20}\text{O}$ , which boils at 109—110° under 12 mm. pressure. It has a sp. gr. 0.8823 at 19.5°/4° and  $n_D$  1.1397 at 19.5°.

With phosphoric oxide, the alcohol yields isobutenyldimethylcyclohexene,  $\text{CH}_2 \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{CMe}_2 \text{---} \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{CMe}_2$ , boiling at 195—196°. It has a sp. gr. 0.8246 at 23°/4° and  $n_D$  1.4653.

isoButenyldimethylcyclohexenylamine,



obtained by reducing the oxime, boils at 108—112° under 14 mm. pressure. A by-product is an oil boiling at 150—160° under 10 mm. pressure. The base is unstable, decomposing slowly with formation of ammonia. The sulphate,  $\text{C}_{12}\text{H}_{21}\text{N} \cdot \text{H}_2\text{SO}_4$ , melts at 115—116°, and the phenylthiocarbamide at 129—130°. J. J. S.

**Condensation Products of High Molecular Weight from Acetone.** Alkaline Condensation of Acetone. EMIL KNOEVENAGEL and LEO BLACH (*Ber.*, 1906, 39, 3451—3457).—isoButenyldimethylcyclohexenone (compare preceding abstract) yields acetone and isoacetophenone when boiled with concentrated formic acid. Two products, isomeric with isobutenyldimethylcyclohexenone, have been prepared from the higher fractions obtained by the action of sodium ethoxide on acetone. The first,  $\alpha$ -isoxylitone is identical with Kerp and Müller's xylitone. It boils at 117—119° under 11 mm. pressure, has a sp. gr. 0.9396 at 16°/4° and  $n_D$  1.5249 at 16°; it yields an oily oxime, and a semicarbazone which melts at about 159°. The second compound,  $\beta$ -isoxylitone, distils at 129—131.5° under 11 mm. pressure, has a sp. gr. 0.9513 at 18°/4°,  $n_D$  1.5182 at 18°, and yields a semicarbazone melting at 175°. J. J. S.

**Condensation Products of High Molecular Weight from Acetone.** Acid Condensation of Acetone. EMIL KNOEVENAGEL and HANS BEER (*Ber.*, 1906, 39, 3457—3466. Compare preceding abstracts).—The following fractions have been isolated from the



products of high boiling point obtained by the condensation of acetone with hydrochloric acid: 120—122°, 127—129°, 137—139°, and 141—144°, all under a pressure of 11 mm. The first fraction has the composition  $C_{15}H_{24}O_2$  and yields a semicarbazone which melts at 148°. The fraction 127—129° appears to be identical with Pinner's xylitone (Abstr., 1882, 941). With semicarbazide it yields a derivative melting at 151°, and oily products with hydroxylamine or phenylhydrazine. It is not identical with synthetical xylitone or with  $\alpha$ - and  $\beta$ -isoxylitones. The analytical data of fractions three and four agree with the formula  $C_{19}H_{26}O$ .

From a second specimen of Kahlbaum's high boiling products, two fractions, 128—130° and 140—142°, were obtained. The first fraction, after removal of small amounts of oxygenated compound by means of sodium hydrogen sulphite, gave analytical data agreeing with the formula  $C_{15}H_{24}$ . It has a sp. gr. 0.9062 at 16°/4° and  $n_D$  1.5338, and may probably be a sesquiterpene. The second fraction gives analytical results agreeing with either  $C_{18}H_{30}$  or  $C_{21}H_{36}$ . J. J. S.

**Nitro- and Amino-propio-phenones.** EZIO COMANDUCCI and LUIGI PESCIPELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 286—291).—By the action of fuming nitric acid on propio-phenone under various conditions, the authors have obtained the three nitro-propio-phenones.

*o*-Nitropropio-phenone (?),  $NO_2 \cdot C_6H_4 \cdot COEt$ , crystallises from alcohol in yellow needles melting at 85°, and is soluble in water, ether, chloroform, or benzene.

*m*-Nitropropio-phenone (?) (compare Barry, Abstr., 1874, 74) crystallises from alcohol in pale, yellow needles melting at 98°, dissolves in water, benzene, ether, chloroform, or light petroleum, and yields a white, crystalline product with sodium hydrogen sulphite.

*p*-Nitropropio-phenone (?) separates from ether in yellowish-white crystals melting at 114°, dissolves rapidly in alcohol, chloroform, benzene, or alkali solution and to a less extent in water or light petroleum, and forms a white, crystalline compound with sodium hydrogen sulphite.

The aminopropio-phenones obtained by reducing the *o*- and *p*-nitro-compounds are white, and dissolve in water, alcohol, or ether, whilst that from the *m*-derivative is a syrup with an odour of strawberries and is soluble in water or alcohol; all of them give the alkaloid reactions. The hydrochloride of the *m*-amino-derivative decomposes at 170° and melts at a slightly higher temperature, whilst those of the ortho- and para-compounds decompose without melting at about 200°. (Compare Kunckell, Abstr., 1900, i, 664.) T. H. P.

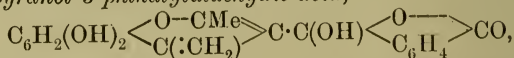
**Migration of the Phenyl Group; Mode of Fixation of Hypoiodous Acid and the Elimination of Hydrogen Iodide.** MARC TIFFENEAU (*Compt. rend.*, 1906, 143, 649—651. Compare Abstr., 1902, i, 666; 1904, i, 63; this vol., i, 662, 724).—Hydrocarbons of the general formula  $RArC:CHR'$  (where R and R' represent alkyl groups which may be identical or different or replaced by

hydrogen, and Ar represents an aryl group) form iodohydrins, which, on treatment with silver nitrate, are converted into the ketones,  $R \cdot CO \cdot CHArR'$ . Thus,  $\alpha$ -phenyl- $\Delta^{\alpha}$ -isoamylene,  $CHPh:CHPr^{\beta}$ , boiling at  $204-206^{\circ}$ , yields  $\alpha$ -phenylisovaleraldehyde,  $CHPhPr^{\beta} \cdot CHO$ , boiling at  $222-223^{\circ}$ .  $\beta$ -Phenyl- $\Delta^{\alpha}$ -amylene,  $CH_2:CPhPr^{\alpha}$ , boiling at  $198-200^{\circ}$ , and having a sp. gr. 0.9138 at  $0^{\circ}$ , yields benzyl propyl ketone,  $CH_2Ph \cdot COPr^{\alpha}$  (Blaise, Abstr., 1902, i, 164), which boils at  $237-239^{\circ}$ , has a sp. gr. 0.9889 at  $0^{\circ}$ , and forms a semicarbazone melting at  $189^{\circ}$ .  $\beta$ -Phenyl- $\Delta^{\beta}$ -butylene,  $CPhMe:CHMe$ , yields benzyl methyl ketone which has a sp. gr. 0.997 at  $0^{\circ}$  (Darzens, this vol., i, 63).  $\beta$ -Phenyl- $\Delta^{\beta}$ -amylene,  $CPhMe:CHEt$ , boiling at  $199-201^{\circ}$ , yields  $\alpha$ -phenyl-propyl methyl ketone,  $CHPhEt \cdot COMe$ , which boils at  $225-227^{\circ}$ , has a sp. gr. 0.979 at  $0^{\circ}$ , and forms a semicarbazone melting at  $188^{\circ}$ .

The iodohydrin of  $\alpha$ -phenyl- $\Delta^{\alpha}$ -isobutylene,  $CHPh:CMe_2$ , when treated with silver nitrate, yields a mixture of phenylisobutaldehyde (Abstr., 1902, i, 666), and phenylbutylene oxide,  $O \begin{smallmatrix} \text{CHPh} \\ \diagup \\ \text{CMe}_2 \end{smallmatrix}$ , which boils at  $213-215^{\circ}$ ; it is probable that in the case of this hydrocarbon the two iodohydrins,  $CHPhI \cdot CMe_2 \cdot OH$  and  $OH \cdot CH \cdot Ph \cdot CMe_2$ , are formed, which, on elimination of hydrogen iodide, yield the corresponding ethylene oxide and unstable vinyl alcohol respectively, the latter changing into the isomeric aldehyde. M. A. W.

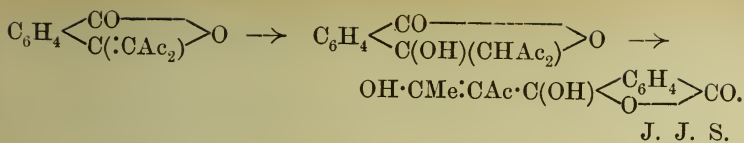
[*p*-Dimethylaminobenzylideneacetone.] Correction. FRANZ SACHS and WILLY LEWIN (*Ber.*, 1906, 39, 3785).—*p*-Dimethylaminobenzylideneacetone sinters at  $130^{\circ}$  and melts at  $134-135^{\circ}$  and not at  $230^{\circ}$  and  $234-235^{\circ}$  as given previously (Abstr., 1903, i, 37. Compare Rupe and Siebel, this vol., i, 859). G. Y.

Combination of Phthalylacetylacetone with Pyrogallol. CARL BÜLOW and MAX DESENISS (*Ber.*, 1906, 39, 3664—3667. Compare Abstr., 1901, i, 475; 1902, i, 554; 1905, i, 149, 294, 529; this vol., i, 588).—The lactone of 7:8-dihydroxy-2-methyl-4-methylene-1:4-benzopyranol-3-phthalylaldehydic acid,



is obtained in the form of its hydrochloride by passing hydrogen chloride into an acetic acid solution of pyrogallol and phthalylacetylacetone and keeping the mixture at  $0^{\circ}$ . The hydrochloride,  $C_{19}H_{14}O_6 \cdot HCl \cdot 1.5H_2O$ , crystallises from alcohol containing hydrogen chloride in red prisms, which decompose at about  $109^{\circ}$ . It dissolves in acetone, alcohol, benzene, or glacial acetic acid, but is insoluble in ether, and is readily hydrolysed by water. The picrate,  $C_{25}H_{17}O_{13}N_3$ , forms red crystals decomposing at  $195-200^{\circ}$ , and soluble in water and most organic solvents.

It is suggested that in the above condensation the phthalylacetylacetone forms an additive compound with water, and this then passes into the enolic form,



**Sodium Hyposulphite as a Reducing Agent.** II. EUGÈNE GRANDMOUGIN (*Ber.*, 1906, 39, 3561—3564. Compare this vol., i, 716).—In many reductions the use of sodium hyposulphite is to be preferred to that of the usual reducing agents, as in the preparation of  $\beta$ -naphthaquinone from Orange II. (Grandmougin and Michel, *Abstr.*, 1892, 861), or of 1:4-diaminonaphthalene from 4-benzeneazo-1-naphthylamine (Bamberger and Schieffelin, *Abstr.*, 1889, 495).

Sodium hyposulphite may be used in the reduction of compounds other than those containing an azo-group. Nitrobenzene gives poor yields of aniline; *o*-nitrophenol is reduced to *o*-aminophenol; in these cases sodium sulphide is a better reducing agent than the hyposulphite. The quinones: benzoquinone,  $\beta$ -naphthaquinone, and phenanthraquinone, are readily reduced by sodium hyposulphite to the corresponding quinols; oxanthranol is obtained more readily by reduction of anthraquinone in this manner than by Graebe and Liebermann's method (this Journal, 1872, 25, 139).

Benzil is reduced by sodium hyposulphite to benzoin.

G. Y.

**Oxidation of Diaminophenols.** FRIEDRICH KEHRMANN and H. PRAGER (*Ber.*, 1906, 39, 3437—3441).—When a solution containing 2:4-diaminophenol hydrochloride and ferric chloride is mixed with sodium dichromate solution, greenish-black, glistening crystals of *aminobenzoquinoneimide dichromate*,  $2\text{NH}:\text{C}_6\text{H}_3(\text{NH}_2):\text{O} \cdot \text{H}_2\text{Cr}_2\text{O}_7$ , are deposited. They dissolve to a certain extent in cold water, yielding a red solution and are completely decomposed by hot water. The *picrate*,  $\text{C}_{12}\text{H}_9\text{O}_8\text{N}_5$ , forms chocolate-brown crystals.

Corresponding salts of benzoquinoneimides have been obtained from 2:4-diamino-*o*-cresol; the *nitrate*,  $\text{NH}:\text{C}_6\text{H}_2\text{Me}(\text{NH}_2):\text{O} \cdot \text{HNO}_3$ , is readily obtained on the addition of solid sodium nitrate to a mixture of diaminocresol hydrochloride and ferric chloride. It dissolves in water or alcohol, yielding solutions with a bluish-red colour. The *dichromate* and *picrate* have also been prepared.

The *nitrate* of amino-*m*-methylbenzoquinoneimide forms blackish-red needles readily soluble in water; the *dichromate* is readily soluble; the *mercurichloride* is sparingly soluble, and crystallises in blackish-red needles.

Corresponding reddish-violet salts have been obtained from diaminothymol.

J. J. S.

**1:4-Anthraquinone.** C. HASLINGER (*Ber.*, 1906, 39, 3537—3538. Compare Dienel, this vol., i, 290).—The melting point of 1:4-anthraquinone formerly given as  $206^\circ$  must be regarded as a decomposition point, owing to the darkening of the substance which occurs even at  $190^\circ$ . The successive stages of the process of converting 1:4-anthraquinone into quinizarin take place very readily, the diacetylquinizarin



being hydrolysed by cold concentrated acid instead of alcoholic potash as formerly described. G. T. M.

**Preparation of Alkylated Aryl-*p*-diaminoanthraquinone-sulphonic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 174131).—It has been found that the alkyl sulphates behave both as alkylating and sulphonating agents towards the aryldiamino-anthraquinones, so that alkylated aryl-*p*-diaminoanthraquinonesulphonic acids are obtained in one operation.

1-Amino-4-*p*-toluidinoanthraquinone is in this way converted into the colouring matter 4-*p*-toluidino-4-dimethylaminoanthraquinonesulphonic acid and 1:5-diamino-4:8-di-*p*-toluidinoanthraquinone furnishes 4:8-di-*p*-toluidino-1:5-tetramethyldiaminoanthraquinonesulphonic acid which is isolated in the form of its sodium salt. G. T. M.

**Derivatives of the Aminoalizarins.** GUSTAV SCHULTZ and J. ERBER (*J. pr. Chem.*, 1906, [ii], 74, 275—296. Compare Abstr., 1902, i, 299).—The  $\alpha$ -diacetylaminoalizarin melting at 205° crystallises from alcohol in glistening, golden-yellow needles, decomposes when sublimed, forming acetic acid and a red sublimate of  $\alpha$ -aminoalizarin.

$\alpha$ -Dibenzoylaminoalizarin melts above 310°, and gives a red coloration with concentrated sulphuric acid.

$\beta$ -Dibenzoylaminoalizarin gives a dark violet coloration with, but does not dissolve in, aqueous sodium hydroxide, becoming yellow again on addition of hydrochloric acid, and is then soluble in cold sodium hydroxide, forming a bluish-violet solution. With concentrated sulphuric acid it gives a red coloration, and after five minutes on addition of water yields *benzoyl- $\beta$ -aminoalizarin*,  $C_{21}H_{13}O_5N$ , which crystallises from nitrobenzene in small, matted, dark green needles, melts at 275°, sublimes with partial decomposition forming yellow needles, is not hydrolysed by boiling concentrated hydrochloric acid, and gives with concentrated sulphuric acid a red, with aqueous sodium hydroxide a blue, coloration.

Prolonged action of concentrated sulphuric acid on the  $\beta$ -dibenzoylamino-derivative leads to the formation of a *product* which crystallises from nitrobenzene in yellowish-brown needles, melts at 320°, and closely resembles the monobenzoyl derivative.

$\alpha$ -Diazoalizarin sulphate (compare Brasch, Abstr., 1891, 1077) is formed by the action of sodium nitrite on  $\alpha$ -aminoalizarin in ice-cooled, concentrated sulphuric acid solution; it separates on moderate dilution with alcohol in glistening, yellowish-brown needles, decomposes at about 140°, dissolves in much alcohol forming a brownish-violet solution becoming orange-yellow when heated, and when treated with aqueous alkali hydroxides at the ordinary temperature forms a reddish-violet solution which evolves nitrogen and becomes blue, the diazo-sulphate being converted into alizarin. When sublimed or boiled with dilute acids it yielded purpurin (Farbwerke vorm. Meister, Lucius, and Brüning, D.R.-P. 97688). The  $\alpha$ -diazo-hydroxide is obtained as a brown, insoluble residue on treatment of the diazo-sulphate with water.

Diazotisation of  $\beta$ -aminoalizarin leads to the formation of the  $\beta$ -diazosulphate, which separates to a small extent in yellow crystals. On addition of water or alcohol to the acid solution, the  $\beta$ -diazohydroxide,  $C_{14}H_5O_2(OH)_2 \cdot N_2 \cdot OH$ , is thrown down as a scarlet or orange-red precipitate; this darkens on exposure to air, decomposes at  $135^\circ$ , and detonates when heated. It is decomposed by boiling dilute acids, aqueous alkali hydroxides, or alcohol, forming alizarin, only after prolonged drying or contact with dilute sulphuric acid.

With potassium iodide the diazo-derivatives of alizarin form iodoalazarins which dye mordanted stuffs brown. Azo-dyes cannot be obtained by coupling  $\alpha$ -diazalizarin sulphate in alkaline or acid solution, whilst only a small amount of an unstable dye is formed by coupling  $\beta$ -diazalizarin hydroxide with R-salt in alkaline solution.

Experiments are quoted to show that the stability of the diazo-derivatives of benzene and naphthalene increases with the size of the nucleus; it was to be expected, as is found, that the diazo-derivatives of anthracene would be still more stable.  $\beta$ -Diazalizarin hydroxide resembles to some extent the diazonaphthalenes; in the  $\alpha$ -derivatives the characteristics of the diazo-compounds are still less prominent.

When heated with sulphuric acid containing 20—40 per cent. of the anhydride, and poured into water,  $\alpha$ -aminoalizarin yields a reddish-brown precipitate which, when boiled with water, is converted into  *$\alpha$ -aminoalizarin-3-sulphonic acid* (*4-amino-1:2-dihydroxyanthraquinone-3-sulphonic acid*),  $C_{14}H_4O_2(OH)_2(NH_2) \cdot SO_3H$  (D.R.-P. 82938); this crystallises from alcohol in microscopic, nodular aggregates, is almost insoluble in ether, and forms a dark violet, insoluble *barium* salt, and a *silver* salt crystallising in microscopic, reddish-brown needles. Oxidation of the sulphonic acid leads to the formation of phthalic acid. When diazotised and heated in concentrated acid solution at  $50$ — $60^\circ$ ,  $\alpha$ -aminoalizarin-3-sulphonic acid yields *purpurin-3-sulphonic acid*, which is isolated in the form of its sparingly soluble *potassium* salt,  $C_{14}H_7O_8SK$ , and is probably identical with the acid obtained by sulphonation of purpurin or by oxidation of alizarinsulphonic acid with nitric acid (D.R.-P. 84774), together with alizarin-3-sulphonic acid, which is considered to be identical with the acid formed by the action of fuming sulphuric acid on alizarin.

Purpurin-3-sulphonic and alizarin-3-sulphonic acids are formed also by boiling diazotised 4-aminoalizarin-3-sulphonic acid with aqueous sodium hydroxide. G. Y.

**Preparation of a Base,  $C_{10}H_{17}ON$ , from Pulegone.** FRIEDRICH W. SEMMLER (D.R.-P. 173775).— *$\alpha$ -Anhydropulegonehydroxylamine*,  $C_{10}H_{17}ON$ , produced by warming pulegonehydroxylamine with concentrated hydrochloric acid at  $100^\circ$ , when purified by means of its picrate, boils at  $91^\circ$  under 8 mm. pressure. The new base readily takes up four hydrogen atoms, and the resulting tetrahydro-base,  $C_{10}H_{21}OK$ , gives a characteristic thiocarbamide melting at  $132^\circ$ .

*Benzylidene- $\alpha$ -anhydropulegonehydroxylamine*,  $CHPh \cdot C_{10}H_{15}ON$ , obtained by condensing the  $\alpha$ -anhydro-base with benzaldehyde in the presence of sodium ethoxide, crystallises from ether in needles melting at  $105$ — $106^\circ$ ; its picrate melts at  $125$ — $126^\circ$ .

By the action of hydriodic acid on pulegonehydroxylamine, reduction and dehydration occur simultaneously, and a new base is obtained having the composition  $C_{10}H_{19}ON$ . G. T. M.

**Chlorohydrochlorides of Pinene and Firpene.** GEORGE B. FRANKFORTER and FRANCIS C. FRARY (*J. Amer. Chem. Soc.*, 1906, 28, 1461—1467).—The pinene used in these experiments was prepared from ordinary turpentine by distilling with steam, drying, and redistilling until it boiled constantly at  $156\text{--}157^\circ$ ; it had a sp. gr. 0.8647 at  $20^\circ$ ,  $n_D$  1.46336 at  $20^\circ$ , and  $[\alpha]_D +14.34^\circ$ . The firpene was obtained from the western fir by distilling the crude pitch with steam and redistilling the terpene several times; the product had the composition  $C_{10}H_{16}$ , and differed from pinene in both chemical and physical properties. It boiled at  $153\text{--}153.5^\circ$  and had a sp. gr. 0.8598 at  $20^\circ$ ,  $n_D$  1.47299 at  $20^\circ$ , and  $[\alpha]_D -47.2^\circ$ . A method is described for the preparation of the hydrochlorides of these terpenes.

*Pentachloropinene hydrochloride*,  $C_{10}H_{11}Cl_5 \cdot HCl$ , obtained by treating a chloroform solution of pinene hydrochloride with potassium permanganate and hydrochloric acid, forms deliquescent, isometric crystals and melts at  $173\text{--}174^\circ$ . An attempt to prepare the compound from pinene itself instead of the hydrochloride was unsuccessful.

*Nonachloropinene hydrochloride*,  $C_{10}H_7Cl_9 \cdot HCl$ , obtained by the action of chlorine in bright sunlight on a solution in carbon tetrachloride of an uncrystallisable substance formed in the preparation of pentachloropinene hydrochloride, crystallises from alcohol, melts at  $263\text{--}264^\circ$  (uncorr.) and is very soluble in ether, benzene, chloroform, or carbon tetrachloride.

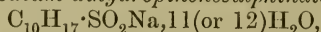
*Firpene hydrochloride*,  $C_{10}H_{16} \cdot HCl$ , melts at  $130\text{--}131^\circ$ , and is more volatile than pinene hydrochloride and more soluble in most of the ordinary solvents.

*Dichlorofirpene hydrochloride*,  $C_{10}H_{14}Cl_2 \cdot HCl$ , is less volatile and less soluble in alcohol than firpene hydrochloride.

*Firpene hydrobromide*,  $C_{10}H_{16} \cdot HBr$ , forms feathery crystals and melts at  $102^\circ$ .

By the action of nitrosyl chloride on firpene an oily, uncrystallisable substance is produced. E. G.

**Dihydropinenesulphinic Acid, Dihydropinenecarbithionic Acid, Thioborneol, and Thiocamphor.** JOSEF HOUBEN and HANS DOESCHER (*Ber.*, 1906, 39, 3503—3509. Compare Borsche and Lange, this vol., i, 679).—*Sodium dihydropinenesulphinate*,



prepared by passing sulphur dioxide into an ethereal solution of the magnesium compound of pinene hydrochloride and subsequently neutralising the portion soluble in ether with sodium carbonate, crystallises from water in well-defined, white leaflets having a faint characteristic odour.

*Dihydropinenesulphinic acid*, when set free by sulphuric acid from the foregoing salt, separates as a colourless oil slowly solidifying to needles on cooling in ice-water; it melts at  $64^\circ$  and probably is hydrated. When heated under 12 mm. pressure, it decomposes, yield-



ing small quantities of camphane, and a similar change occurs on distilling it in steam.

Dihydropinenecarbithionic acid, obtained by adding carbon disulphide to the ethereal solution of the magnesium compound of pinene hydrochloride, is a brown oil having a camphoraceous odour; it is extremely decomposable, but yields characteristic metallic salts.

The interaction of sulphur and the magnesium compound of pinene hydrochloride leads to the production of thioborneol together with smaller quantities of dihydrodicamphene, bornyl disulphide, and other substances containing a larger proportion of sulphur.

On oxidation with dilute chromic acid at moderate temperatures, thioborneol is converted almost quantitatively into bornyl disulphide; at higher temperatures the latter decomposes into thioborneol and thiocamphor, so that by working under these conditions all the sulphur compounds obtained from the magnesium compound of pinene hydrochloride can be converted into thiocamphor. On exposure to the air or more rapidly by the action of oxygen, thiocamphor evolves sulphur dioxide and becomes converted into a colourless, odourless substance melting at  $168^{\circ}$ , which is probably bornyl sulphide. G. T. M.

Pitch [Oleo-resin] and Terpenes of the Norway Pine and the Douglas Fir. GEORGE B. FRANKFORDER (*J. Amer. Chem. Soc.*, 1906, 28, 1467—1472).—The wood of the Norway pine (*Pinus resinosa*) yields from 6.2 to 42.6 per cent. of "pitch" [oleo-resin], which is obtained as a colourless, mobile liquid, has a sp. gr. 0.8137,  $n_D$  1.47869,  $[\alpha]_D + 4^{\circ}$ , and consists of about 22.1 per cent. of oil of turpentine, 77.3 per cent. of colophony, and 0.6 per cent. of water. The terpene obtained from this oleo-resin by steam distillation boils at  $153$ — $154^{\circ}$ , has a sp. gr. 0.8636,  $n_D$  1.47127, and  $[\alpha]_D + 17.39^{\circ}$ . The terpene obtained by the process of destructive distillation boils at  $158$ — $160^{\circ}$ , has a sp. gr. 0.8666,  $n_D$  1.4716, and  $[\alpha]_D - 7.56^{\circ}$ .

The wood of the Douglas fir (*Pseudotsuga taxifolia*) contains from 11.6 to 42.4 per cent. of oleo-resin which when first obtained is a clear, colourless liquid, but when left in the air becomes viscous and coloured. This product has a peculiar, aromatic odour, a sp. gr. 0.9821,  $n$  1.51745, and  $[\alpha]_D - 8.82^{\circ}$ , and contains about 22 per cent. of turpentine. The terpene obtained from this oleo-resin by steam distillation boils at  $153.5$ — $154^{\circ}$ , has a sp. gr. 0.8621,  $n_D$  1.47299, and  $[\alpha]_D - 47.2^{\circ}$ . The terpene obtained by destructive distillation boils at  $157$ — $160^{\circ}$ , has a sp. gr. 0.8662,  $n_D$  1.47246, and  $[\alpha]_D - 29.4^{\circ}$ . All the physical constants were determined at  $20^{\circ}$ . E. G.

Volatile Oil of Juniperus Phoenicea. J. RODIÉ (*Bull. Soc. chim.*, 1906, [iii], 35, 922—925. Compare Umney and Bennett, *Pharm. J.*, 75, 827).—The oil is bright yellowish-green and has an odour recalling those of juniper and savin, more especially the former. It is soluble in four to five times its volume of alcohol ( $90^{\circ}$ ), has a sp. gr. from 0.867—0.868 and its rotation in a 100 mm. tube varies from  $2^{\circ}54'$  to  $4^{\circ}10'$ . The yield is from 0.45 to 0.5 per cent. of the plant.

The oil contains 92.3 per cent. of terpenes, principally pinene with

traces of phellandrene and camphene and possibly dipentene, and 6.51 per cent. of other constituents boiling above 180°. T. A. H.

**Oil of Myrrh.** KURT LEWINSOHN (*Arch. Pharm.*, 1906, 244, 412—435. Compare Tschirch and Bergmann, this vol., i, 197).—Three samples of commercial oil were examined, and one that was freshly prepared in the laboratory by distilling heerabol-myrrh with steam without addition of alkali. Three samples, including the fresh one, contained cuminaldehyde up to 1 per cent.; all samples contained small quantities of eugenol and *m*-cresol, and of acetic and palmitic acids, the latter being present as esters in the fresh sample, in the free state in the commercial samples. When one commercial sample, freed from these constituents, was mixed with light petroleum, a resin separated in amount equal to about 30 per cent. of the oil; this contained oxygen, and, when reduced in amyl-alcoholic solution with sodium, yielded a sesquiterpene apparently identical with cadinene. By fractional distillation of the oils over metallic sodium, pinene, dipentene, and limonene were isolated; it is an open question whether the dipentene is present in the original oils.

From one commercial sample, a fourth *terpene*,  $C_{10}H_{16}$ , also was isolated, possibly an intermediate stage between limonene and dipentene; it boils at 78—80° under 20 mm. pressure, has a sp. gr. 0.847 at 20°, and  $[\alpha]_D + 80^\circ$  at 20°; it forms a *tetrabromide* melting at 115°, a *monohydrochloride* melting at 6°, and an oily *nitrosochloride*. Two other, possibly new, *sesquiterpenes*,  $C_{15}H_{24}$ , were isolated also from the other two commercial samples; one, forming 24 per cent. of the oil from which it was obtained, boiled at 151—154° under 15 mm. pressure and had a sp. gr. 0.911 at 21°; the other boiled at 163—168° under 12 mm. pressure, and had sp. gr. 0.926 at 20° and  $[\alpha]_D + 22.75^\circ$  at 20°. C. F. B.

**Preparation of Normal Esters from Santal Oil.** KNOLL & Co. (D.R.-P. 173240).—The disadvantages attending the therapeutic application of santal oil and its known derivatives are overcome by converting the oil into an alkyl carbonate or an ester of an aromatic monobasic acid.

The *benzoyl* derivative of santal oil prepared either by heating the oil with benzoic anhydride at 110° or by condensing it with benzoic chloride in the presence of pyridine, has a sp. gr. 1.047 at 15°, and boils at 236—238° under 15 mm. pressure. This preparation is not volatile in steam and may thus be separated from the unbenzoylated santal oil.

The *salicyl* derivative is made by heating santal oil or pure santalol with salol and a small proportion of sodium hydroxide under diminished pressure until the elimination of phenol is complete; the sp. gr. is 1.07, and the salicylsantalol boils with partial decomposition at 250—260° under 20 mm. pressure.

*Santalyl ethyl carbonate*, prepared by condensing santal oil with ethyl chlorocarbonate in pyridine, boils at 180—185° under 25 mm. pressure, and has a sp. gr. 1.010 at 15°. The interaction of carbonyl chloride and santal oil under these conditions gives rise to the normal santalyl carbonate. G. T. M.

**Baptisia Glucosides.** K. GORTER (*Arch. Pharm.*, 1906, 244, 401—405. Compare Abstr., 1898, i, 39).— $\psi$ -Baptisin has now been isolated from the roots of *Baptisia tinctoria*.

$\psi$ -Baptigenin melts at 303—304°. Its sodium derivative has the composition  $C_{15}H_{11}O_6Na, H_2O$ ; when it is heated at 150° with ethyl iodide and a little alcohol, it is converted partially into a new substance which melts at 169°, contains C 71.3, H 4.9 per cent. ( $C_{12}H_{10}O_3?$ ), dissolves readily in hot alcohol, and gives no coloration with ferric chloride in acetone solution.  
C. F. B.

**Attempts to Prepare Aloe-emodin.** OTTO A. OESTERLE (*Chem. Centr.*, 1906, ii, 882; from *Schweiz. Woch. Pharm.*, 44, 509—512).—Aloetic acid was reduced by means of a very large excess of 33 per cent. potassium hydrogen sulphide to hydroaloetic acid; the latter compound when diazotised and heated with alcohol gave a small quantity of aloe-emodin. *Hydroaloetic acid* is a bluish-black, amorphous powder, which is insoluble in cold water, slightly soluble in hot water or alcohol, and dissolves readily to a deep blue solution in alkali hydroxides or carbonates; it is readily soluble in concentrated sulphuric acid, forming a brownish-yellow solution which, on addition of water, yields the unchanged acid and not a sulphate.  
P. H.

**Elaterin.** JACQUES POLLAK (*Ber.*, 1906, 39, 3380—3382. Compare Thoms, *Chem. Zeit.*, 1906, 923; Berg, this vol., i, 596).—The analytical data for elaterin agree equally well with Zwenger's formula,  $C_{20}H_{28}O_5$ , or with that of Berg,  $C_{28}H_{38}O_7$ . The values obtained for the molecular weight vary considerably. The compound dissolves in alcoholic potash, but is partially decomposed and acetic acid is liberated. The amount of acetic acid produced on hydrolysing with dilute sulphuric acid (11.2 per cent. of acetyl) agrees best with Zwenger's formula.

J. J. S.

**Elaterin.** FRANZ VON HEMMELMAYR (*Ber.*, 1906, 39, 3652—3653. Compare preceding abstract).—The analytical results obtained for elaterin and its bromo-derivative agree best with the formula  $C_{24}H_{34}O_6$ .

Elaterin yields a *di-phenylhydrazone*, and when heated with alcoholic sulphuric acid yields acetic acid and a phenol, *elateridin*,  $C_{22}H_{32}O_5$ . Boiling with potassium hydroxide solution converts elaterin into *elateric acid*.

J. J. S.

**Chlorophyll Absorption.** M. TSVETT (*Chem. Centr.*, 1906, ii, 892—893; from *Ber. Deutsch. bot. Ges.*, 1906, 24, 316—323).—A detailed account of the selective extraction of the various colouring matters in plants by a number of different solvents, together with a description of the method of separating these colouring matters.

P. H.

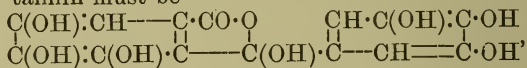
**Kamala and Rottlerin.** HANS TELLE (*Arch. Pharm.*, 1906, 244, 441—458. Compare A. G. Perkin, *Trans.*, 1893, 63, 975; 1895, 67, 230).—Rottlerin, obtained from a commercial specimen of kamala, melted at 203—204°; the empirical formula  $C_{11}H_{10}O_3$  (= 190) and the



molecular weight 486 (determined cryoscopically in naphthalene) were confirmed. When heated for ten minutes with aqueous barium hydroxide solution, saturated in the cold, rottlerin yields 10 to 15 per cent. of phloroglucinol methyl ether, and also resinous substances, whilst some of it is converted into a reddish- or violet-brown isomeride, *ψ-rottlerin*, melting at 235°. When heated for some ten hours with zinc powder and 15 per cent. aqueous sodium hydroxide, rottlerin yields about 60 per cent. of resin and about 30 per cent. of phenols; also a considerable quantity of  $\beta$ -phenylpropionic acid, a little acetic acid, and a small quantity of a crystalline acid which melts at 185—185·5° and contains C 72·4, H 6·4 per cent. From the mixture of phenols, phloroglucinol mono- and di-methyl ethers were isolated. Probably phloroglucinol trimethyl ether was present also, and it was isolated with certainty from a product obtained by using 2 per cent., instead of 15 per cent., aqueous sodium hydroxide; from this product a small quantity of a substance melting at 170—172° and smelling like camphor was isolated.

C. F. B.

**Constitutional Formula of Tannin. Correction.** J. DEKKER (*Ber.*, 1906, 39, 3784. Compare this vol., i, 686).—The constitutional formula for tannin must be



and not as previously given.

G. Y.

**Preparation of Bismuth Tannate.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 172933).—When bismuth hydroxide is heated with a solution of tannin the well known bismuth subtannate,



is produced; when, however, the interaction is effected at the ordinary temperature the *bismuth ditannate*,  $\text{Bi(OH)(O}\cdot\text{C}_{14}\text{H}_9\text{O}_8)_2$ , is obtained. This substance is prepared by adding a solution of bismuth nitrate in dilute nitric acid to a solution of tannin in aqueous sodium carbonate and stirring the mixture for six hours. The product is a pale yellow powder. On boiling with water, the ditannate loses tannic acid and is converted into the monotannate.

G. T. M.

**Brominated 4-Pyrones and their Hydroperbromides.** FRANZ FEIST) *Ber.*, 1906, 39, 3659—3664. Compare Collie and Tickle, *Trans.*, 1900, 77, 1115; Feist and Baum, *Abstr.*, 1905, i, 914; Hantzsch and Denstorff, this vol., i, 745).—*Ethyl hydrogen dibromochelidonate*,  $\text{O} \begin{array}{c} \text{C(CO}_2\text{H)}\cdot\text{CBr} \\ \text{C(CO}_2\text{Et)}\cdot\text{CBr} \end{array} \text{CO}$ , may be obtained from the mother liquors in the preparation of ethyl dibromochelidonate; it crystallises with  $2\text{H}_2\text{O}$  and then melts at 85°, but in the anhydrous state melts at 182—183°.

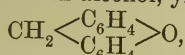
Sulphuryl chloride reacts with a solution of ethyl acetonedioxalate in dry ether, yielding *ethyl dichlorochelidonate*,  $\text{C}_{11}\text{H}_{10}\text{O}_6\text{Cl}_2$ , which crystallises from methyl alcohol in glistening prisms melting at 137—138°. A by-product is *ethyl chlorochelidonate*,  $\text{C}_{11}\text{H}_{11}\text{O}_6\text{Cl}$ , melting at 77°. The separation of the mono- and di-chloro-derivatives is difficult. Iodine reacts

with an acetic acid or acetone solution of ethyl acetonedioxalate, yielding a product free from halogen. It decomposes above  $250^{\circ}$ , is soluble in alkalis, and its analytical data agree with the formula  $C_{14}H_{12}O_{16}$ .  
J. J. S.

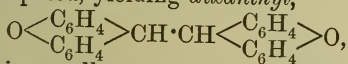
**New Reactions of some Hydrols.** ROBERT FOSSE (*Bull. Soc. chim.*, 1906, [iii], 35, 1005—1017. Compare this vol., i, 691, 756).—

Xanthydrol,  $OH \cdot CH \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle O$ , condenses with hydroxylamine, forming a *product*,  $C_{13}H_{11}O_2N$ , which crystallises in needles, and, on treatment with a solution of hydrogen chloride in alcohol, yields

hydroxylamine hydrochloride and *xanthyl chloride*,  $CH \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle OCl$ , which is unstable and reacts with alcohol, yielding xanthen,

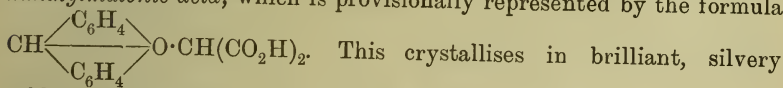


and acetaldehyde. The substance  $C_{13}H_{11}O_2N$  begins to melt at  $140^{\circ}$  and at  $150^{\circ}$  is decomposed, yielding *dixanthyl*,



which crystallises in needles and melts at  $204$ — $205^{\circ}$ . Xanthydrol also reacts with semicarbazide, yielding a *product*,  $C_{14}H_{13}O_2N_3$ , which melts and decomposes at  $170$ — $171^{\circ}$  and reacts with hydrogen chloride in alcohol in much the same way as the oxime described above.

With malonic acid in acetic acid, xanthydrol condenses to form *xanthylmalonic acid*, which is provisionally represented by the formula

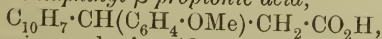


This crystallises in brilliant, silvery tablets, decomposes at  $140^{\circ}$ , forming a green liquid, is decomposed by hydrogen bromide in acetic acid, forming *xanthyl bromide* and malonic acid, and by hydrogen chloride in alcohol, yielding xanthen, acetaldehyde and malonic acid. When heated with pyridine, it furnishes xanthylacetic acid,  $O \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle CH \cdot CH_2 \cdot CO_2H$ , which is not attacked by the halogen acids.

*Dinaphthapyrylmalonic acid*,  $CH \langle \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} \rangle O \cdot CH(CO_2H)_2$ , obtained by the action of malonic acid on dinaphthapyranol or dinaphthapyryl bromide, is decomposed by hydrogen chloride into malonic acid and dinaphthapyryl chloride, and by pyridine into dinaphthapyrylacetic acid and carbon dioxide.

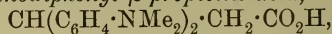
*Xanthylcyanoacetic acid*, similarly obtained, decomposes at  $164$ — $166^{\circ}$ . It is decomposed by hydrogen bromide in acetic acid, yielding xanthyl bromide and cyanoacetic acid, and with pyridine furnishes *xanthylacetone nitrile* which melts at  $140^{\circ}$ .

*p-Methoxyphenyl- $\alpha$ -naphthyl- $\beta$ -propionic acid*,



obtained by condensing malonic acid with *p*-methoxyphenyl- $\alpha$ -naphthyl-carbinol, furnishes a *p-toluidide*, which melts at  $176$ — $177^{\circ}$ . 3 : 4-Methyl-

*enedioxyphenyl- $\alpha$ -naphthyl- $\beta$ -propionic acid*, prepared similarly, melts at 205°. *p*-*Dimethylaminophenyl- $\alpha$ -naphthyl- $\beta$ -propionic acid* melts at 183°. *pp*-*Tetramethyldiaminodiphenyl- $\beta$ -propionic acid*,



obtained from Michler's hydrol, melts at 222°. Triphenylcarbinol, when fused with malonic acid, yields triphenyl- $\beta$ -propionic acid. Cyanoacetic acid condenses with *p*-methoxyphenyl- $\alpha$ -naphthylcarbinol to form an *acid*,  $\text{C}_{21}\text{H}_{17}\text{O}_3$ , and a similar *product* is obtained on condensation with Michler's hydrol. Triphenylcarbinol and cyanoacetic acid gives (1) a *product*,  $\text{C}_{22}\text{H}_{17}\text{O}_2\text{N}$ , which crystallises in colourless needles and melts and decomposes at 155°, and (2) a neutral, nitrogenous *substance* which melts at 114—115°. Benzhydrol reacts with cyanoacetic acid to form a nitrogenous *compound*, insoluble in acids, which melts at 144—155°.

[With N. ROBYN.]—A large number of inorganic salts of the above acids have been prepared and analysed. The condensation products of these with  $\beta$ -ketonic esters (this vol., i, 756), when heated with acetic acid in a closed tube, yield ketones, thus ethyl xanthylacetoacetate furnishes *xanthylpropanone*,  $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{COMe}$ , which crystallises from light petroleum in slender needles and melts at 101—102°. *Xanthylacetophenone*, similarly obtained from ethyl xanthylbenzoylacetate, forms small, white crystals and melts at 83—84°.

[With M. BAILLON.]—*Xanthylacetanilide* forms long, silky needles and melts at 213—214°. *Xanthylaceto-o-toluidide* crystallises in slender needles and melts at 215—216°; the *meta*-isomeride melts at 153—154°, and the *para*-compound at 204—205°. *Xanthylaceto- $\alpha$ -naphthalide* melts at 210—211°, and the  *$\beta$ -isomeride* at 225—216°.

T. A. H.

**Alkaloids of Calumba Root.** JOHANNES GADAMER (*Arch. Pharm.*, 1906, 244, 255—256. Compare Abstr., 1903, i, 50).—An introduction to the following paper, and to one by K. Feist that will appear shortly.

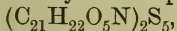
C. F. B.

**Alkaloids of Calumba Root.** E. GÜNZEL (*Arch. Pharm.*, 1906, 244, 257—269. Compare Gadamer, Abstr., 1903, i, 50).—From an alcoholic extract of the root the alcohol was distilled; the residue was diluted with a little water and much alcohol; ether was added, producing a viscid precipitate; the solution was filtered and evaporated, and the residue dissolved in water and shaken with ether, which dissolved fatty substances and columbine. The aqueous liquid was freed from alcohol and ether by heating, clarified with kieselguhr, and precipitated with potassium iodide; from the precipitate the *iodide* melting at 210°, of an alkaloid "B" was extracted by boiling with alcohol, and columbamine iodide remained.

*Columbamine iodide*, probably,  $\text{C}_{21}\text{H}_{22}\text{O}_5\text{NI} = \text{C}_{17}\text{H}_{10}\text{ONI}(\text{OMe})_4$ , is yellow and melts at 224°; the corresponding *chloride* crystallises with  $2\frac{1}{2}\text{H}_2\text{O}$  in yellow needles melting at 194°, and with  $4\text{H}_2\text{O}$  in brown prisms melting at 184°; the *hydrogen sulphate* melts at 220—222°; a



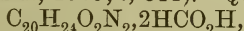
crystalline aurichloride, platinichloride, and nitrate were prepared but not analysed; a greenish-black crystalline pentasulphide,



melting at  $139^\circ$ , was obtained from the iodide by the action of yellow aqueous ammonium sulphide (compare Schreiber, *Arch. Pharm.*, 1890, 228, 631; *Abstr.*, 1890, 1012). The iodide is reduced in aqueous solution by zinc and sulphuric acid to the iodide of a base  $\text{C}_{21}\text{H}_{25}\text{O}_5\text{N} = \text{C}_{17}\text{H}_{13}\text{ON}(\text{OMe})_3$ , *tetrahydrocolumbine*, which melts at  $142^\circ$  and is sensitive to light and air; the *platinichloride* of this mono-acid base melts at  $228^\circ$ ; the chloride and aurichloride, the latter melting at  $201^\circ$ , were prepared but not analysed.

C. F. B.

**Quinine Formates.** P. GUIGUES (*J. Pharm. Chim.*, 1906, [vi], 24, 301—302. Compare *Abstr.*, 1905, i, 811).—*Quinine formate*,



obtained by neutralising a solution of quinine or quinine sulphate in excess of dilute formic acid with ammonia solution, is very soluble in water, melts below  $100^\circ$ , and loses some formic acid.

A *basic quinine formate*,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot \text{HCO}_2\text{H}$ , is obtained by dissolving quinine in the requisite quantity of formic acid and adding ammonium formate to the solution. This does not decompose when heated at  $100^\circ$  and dissolves in less than 20 parts of water.

T. A. H.

**New Salt of Quinine.** LUIGI SANTI (*Chem. Centr.*, 1906, ii, 1205—1206; from *Boll. Chim. Farm.*, 1906, 45, 557—560).—On mixing together ethereal solutions of pure quinine,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot 3\text{H}_2\text{O}$ , and of acetylsalicylic acid and leaving the mixture for twelve hours, a quantitative yield of a salt is obtained which has the composition  $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \cdot \text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$ . This substance which is insoluble in ether but dissolves readily in alcohol or chloroform melts at  $157^\circ$ . P. H.

**Thioquinine and Thiocinchonine.** EZIO COMANDUCCI and LUIGI PESCIPELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 280—285).—*Thioquinine*,  $(\text{C}_{20}\text{H}_{23}\text{ON}_2)_2\text{S}$ , prepared by the action of phosphorus pentasulphide on quinine in chloroform solution, separates from alcohol as a yellow, micro-crystalline powder melting at  $150$ — $152^\circ$  and is soluble in chloroform and sparingly so in ether. It has an odour resembling that of onions and it dissolves in nitric or sulphuric acid, giving a blue fluorescence. With chlorine or bromine water and ammonia it gives the thalleioquinine reaction, and with chlorine water, potassium ferrocyanide, and ammonia it yields a red coloration. When dissolved in dilute sulphuric acid and treated with acetic acid, alcohol, and tincture of iodine, it gives the herapathite reaction. In boiling chloroform solution, it has the normal molecular weight.

*Thiocinchonine*,  $(\text{C}_{19}\text{H}_{21}\text{N}_2)_2\text{S}$ , prepared by the action of phosphorus pentasulphide on cinchonine, is deposited from alcohol as an amorphous powder having an odour like that of garlic, and decomposes, without melting, at about  $130^\circ$ . It dissolves in chloroform, in which it exhibits normal ebullioscopic behaviour, and, to a slight extent, in ether.

T. H. P.

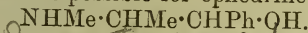
**Extraction of Coca Leaves.** ANNE W. K. DE JONG (*Rec. trav. chim.*, 1906, 25, 311—329. Compare Abstr., 1905, ii, 778; this vol., ii, 315, 625).—In the industrial process for the extraction of the alkaloids from Peruvian coca leaves, the leaves in a fine state of division are treated with a mixture of dilute sodium carbonate solution and petroleum, the petroleum solution of the alkaloids is then neutralised with dilute hydrochloric acid, and the aqueous solution of the hydrochlorides of the alkaloids decomposed by sodium carbonate and the alkaloids extracted by petroleum. The author finds that the best results are obtained when ammonia is used instead of sodium carbonate, and ether instead of petroleum in the above method of extraction; from an exhaustive series of experiments (for details of which the original must be consulted) it is shown that the percentage of the total alkaloid extracted depends on: (1) the action of excess of sodium carbonate, ammonia, or hydrochloric acid on the alkaloids, (2) the solubility of the alkaloids in the petroleum, (3) the quantities of sodium carbonate and of water, (4) the quantity of petroleum and the duration of the extraction, (5) the state of division of the leaves, and (6) the quantities of hydrochloric acid and sodium carbonate or ammonia employed in the last stage of the process. Comparative experiments conducted on fresh leaves and dried leaves showed that whilst 3 kilos. of the fresh leaves yielded 6.65 grams of alkaloids, the same weight of leaves after drying yielded 10.65 grams. M. A. W.

**Ephedrine and  $\psi$ -Ephedrine.** ERNST SCHMIDT and HERMANN EMDE (*Arch. Pharm.*, 1906, 244, 241—255).— $\psi$ -Ephedrine, obtained from ephedrine (E. Schmidt, this vol., i, 602), was found to be identical with the natural base in rotation ( $[\alpha]_D$  51.2° at 20°, in 0.5 per cent. alcoholic solution) and crystalline form (rhombic system;  $a:b:c = 0.843:1:1.858$ ). Ephedrine undergoes a partial transformation when it is heated by itself at 100°, or with aqueous sodium carbonate.

When  $\psi$ -ephedrine is heated with methyl-alcoholic methyl iodide it is converted partially into oily *methyl- $\psi$ -ephedrine*, the *aurichloride* of which,  $C_{11}H_{17}ON, HAuCl_4$ , melts at 119—123°. When excess of methyl iodide is used, the quaternary *methiodide*,  $C_{12}H_{20}ONI$ , melting at 205°, is obtained in addition; the corresponding quaternary *aurichloride* and *platinichloride* melt at 194—195° and 204—205° respectively. These salts differ distinctly, although often only slightly, from the corresponding salts derived from ephedrine; and the quaternary iodide crystallises in the rhombic system ( $a:b:c = 0.642:1:1.209$ ) whilst the quaternary iodide from ephedrine is rhombic with sphenoidal hemihedry ( $a:b:c = 0.979:1:0.761$ ); again,  $\psi$ -ephedrine hydriodide, melting at 172°, is rhombic and holohedral ( $a:b:c = 0.603:1:1.372$ ), whilst ephedrine hydriodide, melting at 155—156°, although rhombic, is hemihedral ( $0.737:1:0.286$ ).

Methyl- $\psi$ -ephedrine methyl hydroxide, when subjected to prolonged distillation with water, decomposes into trimethylamine and an unsaturated substance,  $C_9H_{10}O$ , which boils at 197—199°. A similar result is obtained with methylephedrine methyl hydroxide, except that the unsaturated substance boils at 212—216°, and possibly is identical with  $\alpha$ -phenylallyl alcohol,  $CH_2:CH \cdot CHPh \cdot OH$ .

A formula suggested as possible for ephedrine is



C. F. B.

*See errata, 1902, p. 1266*

Ergot. FRIEDRICH KRAFFT (*Arch. Pharm.*, 1906, 244, 336—359).—

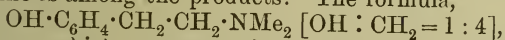
The following substances were isolated: A phytosterol: ergosterol (Tanret). Two alkaloids: ergotinine (Tanret; Keller's "cornutine" and Jakobi's "secaline"); and *hydroergotinine*, which is isomorphous and more soluble. A crystalline  $\delta$ -lactonic acid, *secalonic acid*,  $\text{C}_{14}\text{H}_{14}\text{O}_6$ , which is yellow and melts at  $244^\circ$ ; and the corresponding *hydroxy*-acid, and another acid formed by loss of carbon dioxide, both of which are yellow and amorphous. *Aminosecalesulphonic acid* (Kobert's "ergotic acid"),  $\text{NH}_2 \cdot \text{C}_{15}\text{H}_{27}\text{O}_{15} \cdot \text{SO}_3\text{H}$ . Betaine, choline and man-nitol.

The alkaloids are poisons, causing convulsions and gangrene, but they do not cause the specific action of the drug on the uterus.

C. F. B.

Ergotinine. CHARLES TANRET (*J. Pharm. Chim.*, 1906, [vi], 24, 397—403).—Since ergotinine combines with phenol, the use of the latter as a solvent for cryoscopic determinations of the molecular weight of ergotinine is not permissible (see Barger and Carr, *Pharm. J.*, 1906, [iv], 23, 257). From the analysis of its salts, the formula  $\text{C}_{35}\text{H}_{40}\text{O}_5\text{N}_5$  is deduced. The use of the name ergotoxine, applied by Barger and Carr (*loc. cit.*) to amorphous ergotinine, is objected to. E. F. A.

Hordenine. OTTO GAEBEL (*Arch. Pharm.*, 1906, 244, 435—441. Compare Léger, this vol., i, 204, 761).—Hordenine,  $\text{C}_{10}\text{H}_{15}\text{ON}$ , is oxidised completely by permanganate. If it is methylated by shaking a solution of it in aqueous potassium hydroxide with dimethyl sulphate, and the resulting alkaline solution oxidised with potassium permanganate on the water-bath, anisic acid is obtained. When the methiodide is treated with silver hydroxide, and the quaternary ammonium hydroxide which results is submitted to dry-distillation, trimethylamine is among the products. The formula,



is the only one which expresses these reactions of hordenine satisfactorily.

C. F. B.

Alkaloids of Tobacco. AMÉ PICTET (*Arch. Pharm.*, 1906, 244, 375—389).—A complete account of researches already published (Abstr., 1895, i, 627; 1898, i, 50, 688; 1899, i, 164; 1900, i, 685; 1901, i, 339; 1904, i, 86, 520, 771; 1905, i, 545, 543).

The subjects dealt with are:—Constitution of nicotine; synthesis of nicotine; nicotine; nicotimine; nicotelline; pyrrolidine. C. F. B.

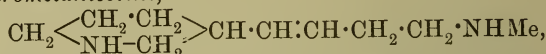
Opium Alkaloids and the Constitution of Berberine and Morphine. FRANZ FALTIS (*Chem. Centr.*, 1906, ii, 1011—1012; from *Pharm. Post*, 39, 497—499).—The author discusses the common origin of the alkaloids papaverine, narcotine, berberine, corydaline, morphine, codeine, thebaine, protopine, glaucine, and chelidonine, and arrives at conclusions different from those of Perkin, Pschorr, and Freund as to the formulæ of berberine and morphine.

P. H.



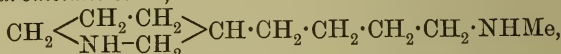
**Reduction of Metanicotine with Sodium and Absolute Alcohol.** II. EMIL MAAS and ADOLF HILDEBRANDT (*Ber.*, 1906, 39, 3697—3702. Compare Abstr., 1905, i, 543).—The product, obtained by reducing metanicotine by means of sodium and absolute alcohol, is not uniform, but a mixture of hexahydrometanicotine and octahydrometanicotine, which may be separated by fractional distillation in a current of steam.

*Hexahydrometanicotine,*

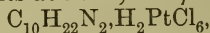


is an oil which boils at 248—250°, has the sp. gr. 0.9578 at 20°/4°, and is volatile with steam. It is optically inactive. The *platini-chloride*,  $\text{C}_{10}\text{H}_{20}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$ , melts and decomposes at 225°.

*Octahydrometanicotine,*



is an oil which boils at 258.5—260°; it is also volatile with steam. It has the sp. gr. 0.9173° at 20°/4°, and is optically inactive. Its *hydrochloride*,  $\text{C}_{10}\text{H}_{22}\text{N}_2 \cdot 2\text{HCl}$ , separates from water in glistening, colourless needles and melts at 202°; the *platinichloride*,

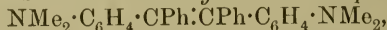


melts and decomposes at 202.5°; the *aurichloride*,  $\text{C}_{10}\text{H}_{22}\text{N}_2 \cdot 2\text{HAuCl}_4$ , melts at 142°. A. McK.

**Solanine Extracted from Solanum sodomæum.** GIUSEPPE ODDO and AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 312—319. Compare this vol., i, 527).—The melting point of solanine varies considerably with the size of the flame by which it is heated, so that it cannot be used as a criterion of purity.

The authors have effected greater purification of solanine by crystallising it several times from 80 per cent. alcohol, then dissolving it in very dilute sulphuric acid, filtering, precipitating by means of alcohol sodium hydroxide and washing with water until all the alkali is removed. After repetition of this process and further crystallisation from alcohol, the solanine obtained gives, on analysis and molecular weight determination in acetic acid, numbers agreeing well with the formula  $\text{C}_{27}\text{H}_{47}\text{O}_9\text{N} \cdot \frac{1}{2}\text{H}_2\text{O}$ . T. H. P.

**Amino-derivatives of Tetraphenylethylene. Quinonoid Compounds.** X. RICHARD WILLSTÄTTER and MAX GOLDMANN (*Ber.*, 1906, 39, 3765—3776).—s-4 : 4'-*Tetramethyldiaminotetraphenylethylene*,



prepared by reduction of *p*-dimethylaminobenzophenone with tin and hydrochloric acid in alcoholic solution, crystallises on addition of ether or light petroleum to its solution in benzene or chloroform in long, glistening, lemon-yellow needles, melts at 224—225°, decomposes above 300°, and gives a deep-red coloration with ferric chloride in acid solutions. The *hydrochloride* and *sulphate* form colourless needles, the dark reddish-brown *mercurichloride* and *platinichloride* are insoluble.

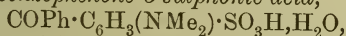
When reduced by means of zinc dust in glacial acetic acid solution, *p*-dimethylaminobenzophenone yields s-4 : 4'-*tetramethyldiaminotetraphenylethyleneglycol*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{OH}) : \text{CPh}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , which crys-

tallises in slender spears, melts and decomposes at 186—187°, becomes yellow on exposure to light, and dissolves in concentrated hydrochloric acid, forming a colourless solution which becomes red slowly at the ordinary temperature or more quickly when heated. When reduced with zinc dust and glacial acetic acid, the pinacone yields tetramethyldiaminotetraphenylethylene and a *substance*, which is obtained also by the action of concentrated sulphuric acid on the pinacone, crystallises in colourless, rhombic and octagonal leaflets, melts at 255—256°, has feeble basic properties, and does not give a coloration with ferric chloride in acid solutions.

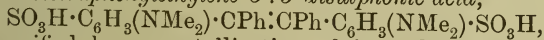
When boiled with absolute alcohol, the pinacone yields a *pinacoline*,  $C_{30}H_{30}ON_2$ , which crystallises in rhombic plates, melts at about 214—217°, and forms a *hydrochloride* crystallising in long, silky, hexagonal leaflets.

*p*-Dimethylaminobenzylhydrol ethyl ether,  $NMe_2 \cdot C_6H_4 \cdot CHPh \cdot OEt$ , prepared by the action of alcohol on the benzhydrol in presence of an acid, crystallises in colourless needles, melts at 37—37·5°, boils at 206—208° under 14 mm. pressure, has a slight odour of benzaldehyde, and gives with hot concentrated hydrochloric acid an intense yellow, with concentrated sulphuric acid an intense red, coloration.

4-Dimethylaminobenzophenone-3-sulphonic acid,



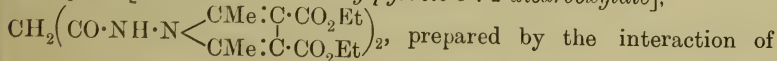
formed by the action of fuming sulphuric acid on the ketone at 130°, separates in large, clear, triclinic crystals [ $a : b : c = 1.1310 : 1 : 2.8296$ ;  $\alpha = 89^\circ 1'5'$ ,  $\beta = 83^\circ 40'$ ,  $\gamma = 77^\circ 31'$ ], loses  $H_2O$  over sulphuric acid, melts and decomposes at 296—298°, forms yellow solutions, has a strong acid reaction, reduces hot ammoniacal silver solution, and decolorises potassium permanganate in alkaline or acid solution. The *barium*, *calcium*, and *silver* salts are described. The *oxime*,  $C_{15}H_{16}O_4N_2S$ , crystallises in glistening, white needles, effloresces on exposure to air, and melts and decomposes at 296—298°. When reduced with tin and concentrated hydrochloric acid, the sulphonic acid yields *s*-4 : 4'-tetramethyldiaminotetraphenylethylene-3 : 3'-disulphonic acid,



which is purified by recrystallisation of its *calcium* salt. The acid crystallises in two modifications: in colourless, rhombic plates or leaflets containing  $2H_2O$  on slow cooling of the aqueous solution; and in long, white needles on rapid separation from the solution. The latter form effloresces on exposure to air. With acid or neutral oxidising agents the disulphonic acid gives an intense blood-red coloration which is destroyed by reducing agents or alkali hydroxides. The *salts* are yellow.

Reduction of Michler's ketone with tin and concentrated hydrochloric acid leads to the formation of octamethyltetra-aminotetraphenylethylene (Gattermann, Abstr., 1896, i, 172). G. Y.

**Condensation Products of the Dihydrazides of Dibasic Acids.** CARL BÜLOW and R. WEIDLICH (*Ber.*, 1906, 39, 3372—3377).—*Ethyl malonyl-bis*-[1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate],



prepared by the interaction of

malonyldihydrazide and ethyl diacetylsuccinate in glacial acetic acid solution, crystallises in bundles of needles melting at  $122^{\circ}$ . *Malonyldiacetyldihydrazide*,  $C_7H_{12}O_4N_4$ , is a white powder melting at  $228^{\circ}$ .

*Diacetophenonemalonyldihydrazone*,

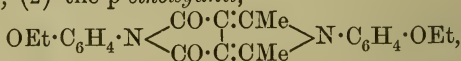


prepared from malonyldihydrazide and acetophenone, melts at  $221^{\circ}$ ; *methyl malonyldihydrazide* melts at  $179^{\circ}$ , and condenses with ethyl diacetylsuccinate to form *ethyl methylmalonyl-bis-[1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate]* melting at  $139-140^{\circ}$ . *Dibenzaldehydethylmalonyldihydrazone* melts at  $249^{\circ}$ , *methyl malonyldiacetyldihydrazide* at  $225^{\circ}$ . Succinyldihydrazide melts at  $166^{\circ}$  (compare Curtius, Abstr., 1895, i, 263), the *diacetyl* derivative at  $233^{\circ}$ . *Ethyl succinyl-bis-[1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate]* melts at  $173^{\circ}$ .

E. F. A.

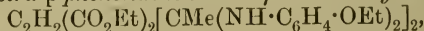
**Action of Ethyl Acetylsuccinate and Diacetylsuccinate on Phenetidine.** LUCIANO ROSSI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 299—308).—When phenetidine reacts with ethyl acetylsuccinate or diacetylsuccinate, the ketonic group of the latter enters into reaction more readily than the carboxyl group, a fact which indicates that these compounds have the enolic structure.

The interaction of ethyl diacetylsuccinate (1 mol.) and phenetidine (1 mol.) yields: (1) *ethyl 1-p-ethoxyphenyl-2:5-dimethylpyrrole-3:4-dicarboxylate*,  $OEt \cdot C_6H_4 \cdot N < \begin{smallmatrix} CMe : C \cdot CO_2Et \\ CMe : C \cdot CO_2Et \end{smallmatrix}$ , which crystallises from alcohol in microscopic, yellow prisms and from acetic acid or benzene in stellar aggregates of needles melting at  $155-156^{\circ}$ ; it has a neutral reaction, dissolves in ether, acetone, or ethyl acetate, gives the pyrrole reaction, and, when dissolved in alcohol, yields an intense blue coloration with ferric chloride; (2) the *p-ethoxyanil*,



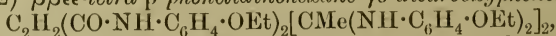
of the foregoing acid; this crystallises from alcohol in tufts of minute, faintly yellow needles melting at  $272^{\circ}$ , and dissolves sparingly in ether, acetone, benzene, acetic acid, or ethyl acetate; it is a neutral substance and gives the pyrrole reaction, but yields no coloration with ferric chloride.

The interaction of 1 mol. of ethyl diacetylsuccinate and 2 mols. of phenetidine yields: (1) the compound melting at  $272^{\circ}$  (*vide supra*) (2) *Ethyl  $\beta\beta\epsilon\epsilon$ -tetra-p-phenetidinoxane- $\gamma\delta$ -dicarboxylate*,



which separates from alcohol as a yellow, microcrystalline powder melting at  $159-160^{\circ}$ , dissolves sparingly in ether, acetone, benzene, ethyl acetate, or acetic acid, and has a neutral reaction.

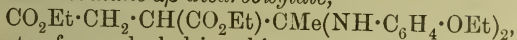
The action of 1 mol. of ethyl diacetylsuccinate on 4 or 6 mols. of phenetidine yields: (1) the compound melting at  $159-160^{\circ}$  (*vide supra*); (2)  *$\beta\beta\epsilon\epsilon$ -tetra-p-phenetidinoxane- $\gamma\delta$ -dicarboxyphenetidine*,



which crystallises from alcohol in white needles melting at  $230^{\circ}$ , dissolves moderately readily in acetone and sparingly in ether, benzene, ethyl acetate, or acetic acid, and has a neutral reaction.



The action of ethyl acetylsuccinate on phenetidine yields: (1) *ethyl  $\gamma$ -di-p-phenetidinobutane- $\alpha\beta$ -dicarboxylate*,



which separates from alcohol in white crystals melting at 114—115°, dissolves in benzene, acetone, or acetic acid, has a neutral reaction, and in cold alcoholic solution gives a green coloration with ferric chloride;

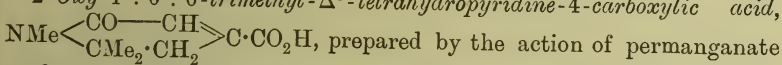
(2)  *$\gamma$ -Diphenetidinobutane- $\alpha\beta$ -dicarboxyphenetide*,

$\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})\cdot\text{CMe}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ , which separates from alcohol in white crystals melting at 230—232°, dissolves sparingly in benzene, acetic acid, or ethyl acetate, and has a neutral reaction.

T. H. P.

**New Acid of the Tetrahydropyridine Series (2-Oxy-1:6:6-trimethyl- $\Delta^3$ -tetrahydropyridine-4-carboxylic Acid).**

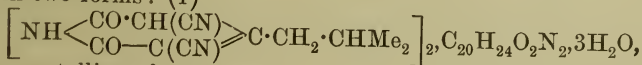
GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1906, 41, 1019—1043). —2-Oxy-1:6:6-trimethyl- $\Delta^3$ -tetrahydropyridine-4-carboxylic acid,



on 3-cyano-1:4:6:6-tetramethylpyridone in neutral solution, crystallises from water in colourless or pale rose-coloured, striated prisms melting at 174—174.5°(corr.), has the normal molecular weight in boiling acetone, and dissolves readily in alcohol, benzene, ethyl acetate, acetic acid, or chloroform, and sparingly in ether. It behaves as a monobasic acid towards alkali hydroxides or carbonates, and, when heated at 290—300°, it evolves methane. It dissolves unchanged in concentrated hydrochloric, sulphuric, or nitric acid, and in aqueous solution it hydrolyses sucrose. It gives with even very dilute ferric chloride solutions an intense blood-red coloration; with dilute ferrous sulphate solution an intense blood-red coloration. The *sodium* (+ H<sub>2</sub>O) and *barium* salts of the acid were analysed. The 3:5-dibromo-derivative, C<sub>9</sub>H<sub>11</sub>O<sub>3</sub>NBr<sub>2</sub>, separates from benzene in colourless, prismatic crystals melting at 137—139°, dissolves slightly in water and gives no red coloration with ferric chloride. The isomeric 5:5-dibromo-derivative crystallises from benzene with  $\frac{1}{2}$ C<sub>6</sub>H<sub>6</sub> in hard, heavy prisms, which effloresce in the air and melt at 201—202°, and its aqueous solution gives a blood-red coloration with ferric chloride; it dissolves readily in alcohol, ether, chloroform, or benzene, and sparingly in carbon disulphide or water, and on heating at its melting point or on boiling with water it loses all its bromine, in the latter case as hydrogen bromide. When heated with potassium hydroxide at 300—320° under a pressure of 40 mm., the acid decomposes, yielding methylamine, oxalic acid, a neutral substance, a syrupy nitrogenous acid, and acrylic acid (?).

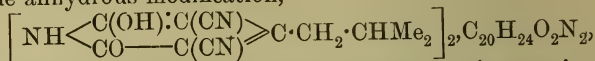
T. H. P.

**Transformations of the Quinine Salt of *iso*Butyldicyanoglutaconimide.** SILVIO ZUBLENA (*Atti R. Accad. Sci. Torino*, 1906, 41, 1044—1053).—The quinine salt of *isobutyldicyanoglutaconimide* exists in two forms: (1)



which crystallises from water in tufts of concentrically-arranged, intensely yellow, slender prisms, and melts and decomposes at about

282°. If this salt, in either the hydrated or the dehydrated form, is suspended in water, it gradually changes into (2) a more stable and less soluble anhydrous modification,



which separates in colourless, probably triclinic, microscopic prisms. This change is accelerated by the action of light. The colourless modification begins to turn yellow at 200°, and, like the yellow form, melts and decomposes at about 282°. A solution of the colourless salt in 60 or 95 per cent. alcohol deposits the yellow modification.

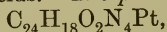
T. H. P.

**Dioximes and similar Compounds.** LEO TSCHUGAEFF (*Ber.*, 1906, 39, 3382—3389; *J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 7—9. Compare Abstr., 1905, i, 743).—The behaviour of different metallic solutions towards the stereoisomeric oximes derived from 2-benzoylpyridine and the oxime of 4-benzoylpyridine (Tschitschibabin, Abstr., 1902, i, 175) has been investigated. The only oxime which give colorations or precipitates is the 2-benzoylpyridineoxime melting at 150—152°, and hence the *syn*-configuration,  $\text{C}_5\text{NH}_5 \cdot \text{C} \cdot \text{Ph}$ , is assigned



to it.

The *palladium* compound,  $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_4\text{Pd}$ , obtained by the action of palladium ammonium chloride on an alcoholic solution of the oxime, crystallises in canary-yellow needles, sparingly soluble in alcohol or ether. It may be recrystallised from chloroform, and is not decomposed by dilute alkalis or weak acids. The *platinum* derivative,



prepared by the action of platinum pyridine chloride on the oxime, forms dark yellow crystals.

Thiele's nitrosoguanidine, represented by the tautomeric formula  $\text{NH} \cdot \text{C}(\text{NH}_2) \text{N} \cdot \text{N} \cdot \text{OH}$ , also yields metallic derivatives. Structural formulæ for the metallic compounds are given.

J. J. S.

**Quinoline Derivatives.** II. Nitration of Quinoline and its Mononitro-derivatives. ADOLF KAUFMANN and HERMAN DECKER (*Ber.*, 1906, 39, 3648—3651. Compare Claus and Kramer, Abstr., 1885, 908; Claus and Hartmann, Abstr., 1896, i, 391; Claus and Schnell, *ibid.*, 319).—6-Nitroquinoline may be further nitrated when heated with the theoretical amount of potassium nitrate and concentrated sulphuric acid at 130—140° for ten hours. The product is a mixture of 5:8-dinitroquinoline and an isomeric compound melting at 185°. The latter dissolves readily in most organic solvents and in dilute sodium hydroxide solution; it does not react with methyl iodide and is readily sublimed.

7-Nitroquinoline is readily nitrated when heated with fuming nitric and concentrated sulphuric acid, the chief product being a new dinitroquinoline melting at 225°. It sublimes readily and dissolves in sodium hydroxide to a characteristic yellow solution. A second product is a dinitro-compound melting at 175°, probably identical with 5:7-dinitroquinoline.

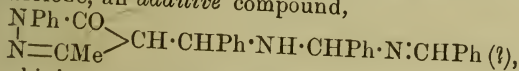
8-Nitroquinoline when boiled for twenty hours with a mixture of

nitric and sulphuric acid, yields 6:8-dinitroquinoline, identical with the product obtained from 2:4-dinitroaniline (La Coste, Abstr., 1882, 979).  
J. J. S.

**Diphenylhydrazones of a Series of Aldehydes.** A. D. MAUREN-BRECHER (*Ber.*, 1906, 39, 3583—3587. Compare Clowes and Tollens, Abstr., 1900, ii, 56).—The *diphenylhydrazones* of the following aldehydes are described; the formulæ and crystalline forms are those of the hydrazones; the temperatures are melting points. Formaldehyde,  $C_{13}H_{12}N_2$ , white plates, 34·5—35°; propaldehyde,  $C_{15}H_{16}N_2$ , long, white needles, 20—21°; butaldehyde,  $C_{16}H_{18}N_2$ , oil; isobutaldehyde, white plates, 30—30·5°; isovaleraldehyde,  $C_{17}H_{20}N_2$ , white plates or prisms, 36—36·5°; o-tolualdehyde,  $C_{20}H_{18}N_2$ , white needles, 103—104°; m-tolualdehyde, light yellow plates, 74—75°; p-tolualdehyde, white needles, 83—84°; cinnamaldehyde,  $C_{21}H_{18}N_2$ , yellow needles, 135—136°; cuminaldehyde,  $C_{22}H_{22}N_2$ , yellow needles, 78·5—79·5°; o-hydroxybenzaldehyde,  $C_{19}H_{16}ON_2$ , colourless needles, 138·5°; m-hydroxybenzaldehyde, yellow needles, 118—119°; vanillin,  $C_{20}H_{18}O_2N_2$ , violet leaflets, 130—131°; piperonal,  $C_{20}H_{16}O_2N_2$ , white plates, 134—135°.  
G. Y.

**Spontaneous Oxidation in presence of Benzaldehyde.** MARIO BETTI (*Gazzetta*, 1906, 36, ii, 427—433).—When dissolved in alcoholic ammonia in presence of a few drops of benzaldehyde or hydrogen peroxide or sodium peroxide, 1-phenyl-3-methyl-5-pyrazolone undergoes oxidation, yielding: (1) rubazonic acid; (2) 1-phenyl-4-benzylidene-3-methyl-5-pyrazolone; (3) 4-benzylidene-bis-1-phenyl-3-methyl-5-pyrazolone,  $CHPh(CH<\begin{smallmatrix} CO-NPh \\ CMe:N \end{smallmatrix})_2$ , which separates in shining, white crystals melting at 167°; the formation of this compound, together with benzaldehyde, from 1-phenyl-4-benzylidene-3-methyl-5-pyrazolone (2 mols.) and water is a reversible reaction. Whether the function of the benzaldehyde in the above reaction is merely to form hydrogen peroxide or some other peroxide or whether it takes part in a cycle of changes, at the end of which it is regenerated, is yet undecided.

On mixing alcoholic solutions of hydrobenzamide and 1-phenyl-3-methyl-5-pyrazolone, an *additive* compound,



is formed in shining, white prisms which turn yellow at 110° and melt and decompose at 125—126°. This compound may also be used in place of benzaldehyde for the oxidation of 1-phenyl-3-methyl-5-pyrazolone.

T. H. P.

**New Additive Compounds of 1-Phenyl-2:3-dimethylpyrazolone (Antipyrine).** FELICE GARELLI and G. A. BARBIERI (*Gazzetta*, 1906, 36, ii, 168—172).—Contrary to Schuyten's statement (Abstr., 1898, i, 92, 452), an aqueous solution of the additive compound of antipyrine with zinc chloride gives a precipitate of zinc sulphide with ammonium sulphide. Solutions of the compounds formed by anti-



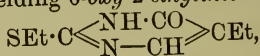
pyrine with mercuric chloride, bromide, and cyanide give the same reactions as solutions of the mercuric haloid salts themselves. With ferric chloride, solutions of all the additive compounds of antipyrine yield the deep red coloration given by solutions of pure antipyrine.

Cryoscopic measurements of various additive compounds of antipyrine in water lead to the following values for the molecular weights, the true values of which are given in brackets: Antipyrine-mercuric cyanide,  $\text{Hg}(\text{CN})_2 \cdot \text{C}_{11}\text{H}_{12}\text{ON}_2$ , 210—222 (440); antipyrine-quinol,  $\text{C}_6\text{H}_4(\text{OH})_2 \cdot 2\text{C}_{11}\text{H}_{12}\text{ON}_2$ , 151—171 (487); antipyrine-resorcinol,  $\text{C}_6\text{H}_4(\text{OH})_2 \cdot \text{C}_{11}\text{H}_{12}\text{ON}_2$ , 140—151 (298); antipyrine-chloral,  $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2 \cdot \text{C}_{11}\text{H}_{12}\text{ON}_2$ , 178—183 (352). In aqueous solution, therefore, these compounds are completely resolved into their components.

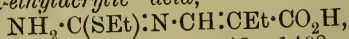
The author is of opinion that the structural formulæ attributed to the double compounds formed by antipyrine have no greater value than the constitutional formulæ proposed for the natural silicates.

T. H. P.

**Pyrimidines. XVIII. 5-Ethylcytosine.** TREAT B. JOHNSON and GEORGE A. MENGE (*J. Biol. Chem.*, 1906, 2, 105—115. Compare Abstr., 1903, i, 526; this vol., i, 704).—*Ethyl sodioformylbutyrate*,  $\text{ONa} \cdot \text{CH} : \text{C} \cdot \text{CO}_2\text{Et}$ , is obtained by the condensation of ethyl formate and ethyl butyrate in the presence of sodium ethoxide. It reacts with  $\psi$ -ethylthiocarbamide, yielding 6-oxy-2-ethylthiol-5-ethylpyrimidine,



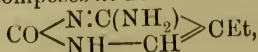
which crystallises from dilute alcohol in well-developed prisms melting at 119—120°. It dissolves readily in alcohol or benzene, but only sparingly in ether. An intermediate product in its formation is  $\beta\psi$ -ethylthiocarbamido- $\alpha$ -ethylacrylic acid,



which crystallises in plates melting at 148—149°; at this temperature carbon dioxide is evolved and the pyrimidine derivative formed.

6-Chloro-2-ethylthiol-5-ethylpyrimidine,  $\text{C}_8\text{H}_{11}\text{N}_2\text{ClS}$ , boils at 160—163° under 24 mm. pressure and is readily converted into the corresponding oxy-derivative. 6-Amino-2-ethylthiol-5-ethylpyrimidine,  $\text{C}_8\text{H}_{13}\text{N}_3\text{S}$ , obtained by the action of alcoholic ammonia on the chloro-derivative at 130—140°, crystallises from a mixture of benzene and light petroleum in prisms melting at 74—76°.

2 : 6-Dioxy-5-ethylpyrimidine (5-ethyluracil),  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CH} \end{array} \text{CEt}$ , is obtained by boiling the oxyethylthiol ethyl derivative with hydrobromic acid; it crystallises in microscopic prisms melting and decomposing at about 300°. One gram dissolves in 625 of water at 25°. 5-Ethylcytosine hydrobromide,  $\text{C}_6\text{H}_9\text{ON}_3 \cdot \text{HBr}$ , obtained by boiling the amino-ethylthioethyl derivative with hydrobromic acid, crystallises in large prisms and melts and decomposes at 284—286°. 5-Ethylcytosine,



crystallises in slender, anhydrous prisms, melts and decomposes at 282—283° and dissolves in about 75 parts of water at 25°. It yields

precipitates with mercuric chloride, phosphotungstic acid and potassium bismuthiodide. The *platinichloride*,  $(C_6H_9ON_3)_2, H_2PtCl_6, 2H_2O$ , dissolves readily in hot water, the *hydrochloride*,  $C_6H_9ON_3, HCl$ , crystallises in flat prisms and melts at  $238-240^\circ$ . The *nitrate* decomposes at  $170-172^\circ$ , and the *picrate* at  $277-278^\circ$ . Mixtures of basic hydrobromides have been obtained.

2:6-Dichloropyrimidine (Gabriel, Abstr., 1905, i, 482) may be obtained by heating 2-thiouracil (Wheeler and Bristol, *ibid.*, i, 483) with phosphorus pentachloride.

J. J. S.

**Preparation of 2-Arylimino-5:5-dialkylbarbituric Acids** FARBERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 172979).—It has been found that the esters of the dialkylmalonic acids will condense with arylguanidines under the influence of alkali alkyl oxides in methyl-alcoholic solution, but not in ethyl alcohol.

2-Phenylimino-5:5-diethylbarbituric acid, produced by condensing phenylguanidine nitrate and ethyl diethylmalonate with sodium methoxide in methyl-alcoholic solution, crystallises from acetic acid and melts at  $249^\circ$ .

2-Phenylimino-5:5-dimethylbarbituric acid, prepared in a similar way from methyl dimethylmalonate, crystallises from alcohol in well-defined needles and melts at  $249-250^\circ$ . 2-p-Tolylimino-5:5-diethylbarbituric acid crystallises in needles and melts at  $239-240^\circ$ . 2-o-Tolylimino-5:5-diethylbarbituric acid and 2-p-chlorophenylimino-5:5-diethylbarbituric acid melt at  $230^\circ$  and  $276-277^\circ$  respectively. These arylimino-derivatives, when hydrolysed with dilute acids, furnish the aromatic amine and the dialkylbarbituric acid.

G. T. M.

**Preparation of Imino-5:5-dialkylbarbituric Acids.** EMANUEL MERCK (D.R.-P. 172980. Compare Abstr., 1905, i, 179).—The imino-dialkylbarbituric acids have already been obtained by condensing carbamide with the esters of cyanodialkylacetic acid in the presence of metallic alkyl oxides. It is now found that the acyl derivatives of carbamide may be employed in this condensation, the condensing agent being sodium alkyl oxide, sodamide, or even metallic sodium.

The sodium derivative,  $CO \begin{smallmatrix} \text{N} \text{Na} \cdot \text{CO} \text{---} \\ \text{NH} \cdot \text{C}(\text{NH}) \end{smallmatrix} > C\text{Et}_2$ , of 4-imino-2:6-dioxy-5:5-diethylpyrimidine is obtained by condensing acetylcarbamide with ethyl cyanodiethylacetate in boiling alcoholic sodium ethoxide; the free pyrimidine is set free by acids. This condensation may also be effected by adding the cyanodialkylacetate to an intimate mixture of acetylcarbamide and sodamide suspended in xylene; the reagents are cooled at first, but finally heated at  $120^\circ$ . After removing the xylene, the product, on treatment with water, yields the sodium derivative of the iminodioxymethylpyrimidine.

G. T. M.

**Preparation of 5:5-Dialkylbarbituric Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 173241).—The 4-imino-6-oxy-2-thio-5:5-dialkylpyrimidines, when treated with an oxidising agent,

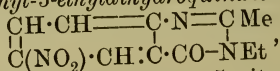
lose their imino-group and sulphur atom, which are replaced by oxygen, so that a 5:5-dialkylbarbituric acid is produced. It is now shown that this substitution may be effected simply by boiling the thio-compound with an acid; the change occurs in two stages, the imino-group being first removed, and then by further action the sulphur is eliminated. Fuming hydrochloric 40 per cent. sulphuric or 70 per cent. acetic acid may be used for this purpose, and in this way 4-imino-6-oxy-2-thio-5:5-dimethylpyrimidine and its diethyl- and dipropyl-homologues may be transformed into dimethyl-, diethyl-, and dipropyl-barbituric acids respectively.

G. T. M.

**Quinazolines. XVI. Synthesis of 6-Nitro-4-keto-2-methyl-dihydroquinazolines from 5-Nitroacetylanthranil and Primary Amines.** MARSTON T. BOGERT and ELLEN P. COOK (*J. Amer. Chem. Soc.*, 1906, 28, 1449—1454. Compare this vol., i, 712, and earlier abstracts.)—5-Nitroacetylanthranil,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C} \begin{smallmatrix} \text{N} \text{Ac} \\ \text{CO} \end{smallmatrix}$ , obtained by the

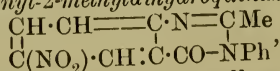
action of acetic anhydride on 5-nitro-acetylanthranilic acid, crystallises in colourless needles and melts at 161—162° (corr.). By the action of dilute aqueous ammonia, it is converted into 6-nitro-4-keto-2-methyl-dihydroquinazoline (6-nitro-4-oxy-2-methylquinazoline), described by Dehoff (Abstr., 1891, 84) and by Thieme (Abstr., 1891, 917). When the anthranil is warmed with methylamine, it is converted into 6-nitro-4-keto-2:3-dimethyldihydroquinazoline (Dehoff and Thieme, *loc. cit.*).

6-Nitro-4-keto-2-methyl-3-ethyldihydroquinazoline,



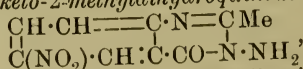
obtained by the action of ethylamine on 5-nitroacetylanthranil, or by the action of ethyl iodide on the sodium derivative of the methylquinazoline, crystallises from alcohol in needles and melts at 166° (corr.).

6-Nitro-4-keto-3-phenyl-2-methyldihydroquinazoline,



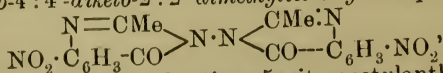
separates from glacial acetic acid in small, pale yellow crystals, melts at 219—220° (corr.), and is sparingly soluble in alcohol.

6-Nitro-3-amino-4-keto-2-methyldihydroquinazoline,



obtained by heating 5-nitroacetylanthranil with hydrazine hydrate in 50 per cent. aqueous solution, crystallises in colourless needles, melts at 208—209° (corr.), and is readily soluble in dilute alcohol. It crystallises from glacial acetic acid with about 2/5 mol. of acetic acid.

6:6'-Dinitro-4:4'-diketo-2:2'-dimethyltetrahydrodiquinazolyl,



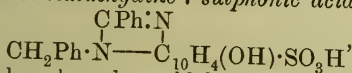
obtained in small yield by heating 5-nitroacetylanthranil (2 mols.) with hydrazine hydrate (1 mol.) in 50 per cent. solution, separates



from glacial acetic acid in small crystals containing 1 mol. of the solvent, and melts and darkens at 281—286°. E. G.

**Preparation of 5-Hydroxynaphthabenzaldehydine-7-sulphonic Acid and its Diamino-derivative.** LEOPOLD CASSELLA & Co. (D.R.-P. 172981).—1:2-Naphthylenediamine condenses with 2 molecular proportions of benzaldehyde to form naphthabenzaldehydine (Abstr., 1906, i, 536), but the reaction does not take place very readily. If, however, a hydroxysulphonic acid of the diamine is employed, the condensation is easily effected even in aqueous solutions.

*5-Hydroxynaphthabenzaldehydine-7-sulphonic acid,*



separates completely when benzaldehyde is added to 5:6-diamino- $\alpha$ -naphthol-3-sulphonic acid suspended in water, the mixture being stirred and heated until all the diamino-acid has disappeared. It is a yellow powder which forms a sodium salt crystallising in leaflets.

3':5'-Diamino-5-hydroxynaphthabenzaldehydine-7-sulphonic acid is obtained directly by substituting *m*-aminobenzaldehyde for benzaldehyde in the foregoing condensation, or is obtained by reducing the corresponding nitro-compound obtained by using *m*-nitrobenzaldehyde in the condensation. On diazotising this diamine, a yellow bis-diazo-compound is produced which develops a red coloration with sodium carbonate solution.

G. T. M.

**Molecular Weight of Indigotin.** WILHELM VAUBEL (*Ber.*, 1906, 39, 3587—3588. Compare Abstr., 1901, i, 714; 1902, i, 110).—On recalculating the molecular weight of indigotin as determined cryoscopically in phenol (*loc. cit.*), with the aid of a correction for the maximum solubility of indigotin in the solvent, but with omission of that previously employed for the supposed absorption of water, the author finds his results to be entirely in agreement with those of Beckmann and Gabel (this vol., i, 900).

G. Y.

**Pyramidone Hydrochloride and Hydrobromide.** CHARLES ASTRE and P. AUBOUY (*Bull. Soc. chim.*, 1906, [iii], 35, 856—858).—*Pyramidone hydrochloride*, obtained by mixing a solution of hydrogen chloride in ether with the base dissolved in the same solvent, forms microscopic, colourless, prismatic crystals, melts at 143—144°, and is very hygroscopic, forming a syrupy acid liquid. The *hydrobromide*, similarly obtained, occurs in colourless, microscopic lamellæ, melts at 170—171°, and is very deliquescent, forming an acid liquid.

T. A. H.

***s*- and *as*-Phenosafuranines.** PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1906, [iii], 35, 858—868. Compare this vol., i, 51).—*s*-Phenosafuranine can be diazotised much more rapidly than *as*-phenosafuranine, and when an aqueous solution of its hydrochloride is shaken with chloroform, the latter does not become coloured as it does when a solution of *as*-phenosafuranine hydrochloride is similarly treated.

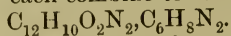
These differences in behaviour may be used to distinguish the two dyes.

The characters and solubilities of the nitrates and oxalates, and of the hydrates formed by the hydrochlorides and sulphates of the two isomerides, and the conditions under which these salts may be obtained are described in detail in the original.

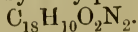
T. A. H.

**Azophenols.** RICHARD WILLSTÄTTER and MAX BENZ (*Ber.*, 1906, 39, 3492—3503. Compare this vol., i, 997).—This paper contains the results of experiments devised to elucidate a curious case of isomerism among the azophenols. The *p*-azophenol obtained by reducing *p*-benzoquinoneazine differs from the substance prepared by the ordinary methods in its colour in the crystalline and powdered condition, in its behaviour towards moist air, and in its solubility in cold benzene. The new modification is denoted by the affix ( $\alpha$ ) and the older form by ( $\beta$ ). It seems probable that these  $\alpha$ - and  $\beta$ -compounds are geometrical isomerides. *p*-Azophenol ( $\alpha$ ) most conveniently prepared by fusing *p*-nitrophenol with potassium hydroxide, crystallises in a mono-hydrated form from ether or alcohol forming pale brown, or amber-yellow plates with blue reflex. The solubility of the hydrated form in benzene at 17° is 1 in 10,800; the anhydrous form separates from this solvent in cruciform aggregates of greenish-brown crystals. The powdered  $\alpha$ -compound assumes a dark yellow colour which becomes green on heating. Both hydrated and anhydrous forms melt and decompose at 215°. A glacial acetic acid solution of hydrogen bromide furnishes blue crystals of the *hydrobromide*,  $C_{12}H_{10}N_2 \cdot HBr$ .

*p*-Azophenol ( $\beta$ ), prepared by reducing *p*-benzoquinoneazine with phenylhydrazine in benzene solution, forms dark red, and reddish-brown leaflets with a blue reflex; when powdered it is brownish-red with a blue tinge, and at 110—140° it assumes a brick-red colour. The solubility of the  $\beta$ -compound in benzene at 17° is 1 in 1500. On heating a portion of the  $\beta$ -compound under reduced pressure a small yield of the green pulverulent anhydrous  $\alpha$ -modification is obtained. The  $\alpha$ -compound is partially converted into the  $\beta$ -modification by heating with moist ether. The two isomerides behave similarly towards dry ammonia gas, yielding anhydrous diammonium salts, which completely dissociate in the air or in the desiccator; they are oxidised with equal readiness by silver oxide, and are equally stable towards phenylhydrazine, with which they each combine to form a crystallisable *salt*,



*o*-Azophenol, when prepared by the potash fusion method from *o*-nitrophenol is accompanied by a by-product, triphenodioxazine,



The *o*-azo-compound takes up 1 mol. of ammonia to form a coffee-brown ammonium salt; if, however, it has been previously melted or distilled in a vacuum, it does not show any tendency to combine with dry ammonia, but regains the power on recrystallisation or exposure to an atmosphere of damp ammonia. *m*-Azophenol, which combines with a proportion varying between 1 and 2 mols. of ammonia, does not react in ethereal solution with silver oxide.

G. T. M.

Derivatives of 5-Azoeugenol and the Constitution of the so-called *o*-Hydroxyazo-compounds. GIUSEPPE ODDO and ERNESTO PUXEDDU (*Gazzetta*, 1906, 36, ii, 1—48. Compare Abstr., 1905, i, 492, this vol., i, 774).—After reviewing the present state of knowledge of the hydroxyazo-compounds, the properties of the following azo-compounds derived from eugenol are discussed at some length. The principal conclusions arrived at are as follows.

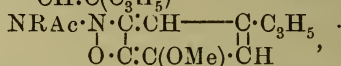
All the azoeugenols are nearly insoluble in cold 0·5 per cent. aqueous sodium hydroxide, but dissolve much more readily in the same liquid at 100°. No change in the boiling point of the sodium hydroxide solution occurs on adding successive quantities of the azo-compound; this behaviour, which is also shown by phenol and  $\alpha$ -naphthol, is held to prove that the azoeugenols yield true sodium salts, which are dissociated to almost the same extent as sodium hydroxide. On cooling the solutions, the sodium salts undergo hydrolysis to the extent of about 58—92 per cent., depending on their structure, the original azoeugenol separating in crystals. No simple connexion can be traced between the degree of hydrolysis of the salts and their solubility. The hydrolysis is held to show that the azoeugenols are pseudo-acids, giving salts only in virtue of a molecular change; they do not redden litmus or combine with ammonia in dry benzene. From their chemical behaviour the free azoeugenols appear to be neither hydrazones nor carbonyl compounds. When boiled with acids or alkalis they do not undergo hydrolysis to form a corresponding quinone; and although they interact vigorously with phenylhydrazine at 110° the product is never a dihydrazone, but always amino Eugenol formed by reduction. Such a reducing action is not observed when ordinary aromatic phenylhydrazones are heated with phenylhydrazine. With hydroxylamine the azoeugenols fail to interact.

The behaviour of the azoeugenols when treated with sodium ethoxide and subsequently with ethyl iodide in alcoholic solution, depends on the nature of the aromatic radicle attached to the azo-group. *o*-Tolueneazoeugenol, *as-m*-xyleneazoeugenol, and *p*-xyleneazoeugenol do not form ethers; these substances contain a methyl radicle in the ortho-position relatively to the azo-group. Benzeneazoeugenol, *m*-tolueneazoeugenol, and *p*-bromobenzeneazoeugenol, give unstable ethers which are at once hydrolysed at the ordinary temperature by 0·5 per cent. aqueous sodium hydroxide. Azoeugenols containing negative elements or radicles in any position (with the exception of *p*-bromobenzeneazoeugenol) give well-defined ethers, which are hydrolysed only by warm sodium hydroxide. The ethers differ entirely from the parent azoeugenols in their behaviour with phenylhydrazine; no action occurs at 110° and very little at 170—180°. In no case is amino Eugenol ethyl ether formed. The ethyl ethers of the azoeugenols appear to have the structure,  $R \cdot N : N \cdot C \begin{smallmatrix} \swarrow C(OEt) \cdot C(OMe) \\ \searrow CH = C(C_3H_5) \end{smallmatrix} > CH$ , of true oxygen ethers.

The acetyl derivatives of the azoeugenols are in all cases easily prepared, and are decomposed only slowly by boiling aqueous sodium hydroxide. Like the parent azoeugenols they interact readily with phenylhydrazine at 110—120°, undergoing reduction to amino Eugenol; acetyl amino Eugenol is never formed. The acetyl derivatives thus differ



entirely from the ethyl ethers, and cannot have an analogous structure; the behaviour with phenylhydrazine is moreover held to exclude the structure  $\text{NRAc} \cdot \text{N} : \text{C} \begin{matrix} \text{CO} \cdot \text{C(OMe)} \\ \text{CH} : \text{C(C}_3\text{H}_5) \end{matrix} \text{CH}$ . The structure



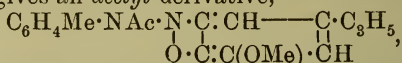
however, is advocated as explaining the properties of the acetyl derivatives.

The parent hydroxyazo-compounds are considered to correspond in structure neither with the alkyl ethers nor with the acetyl derivatives.

The formula,  $\text{R} \cdot \text{N} \begin{matrix} \text{H} \\ \text{H} \end{matrix} \begin{matrix} \text{O} - \text{C} : \text{C(OMe)} \cdot \text{C} \\ \text{N} - \text{C} : \text{CH} - \text{C} \cdot \text{C}_3\text{H}_5 \end{matrix}$ , is attributed to the free

hydroxyazo-compounds, it being assumed that an ordinary single bond can, in certain cases, be divided between two neighbouring elements, as indicated by the sign  $\lessdot$  in the formula. These compounds are termed *mesohydric* and names such as *benzenemesohydrazoeugenol* for benzeneazoeugenol, are given to them.

*o-Toluenazoeugenol* (*o-toluenemesohydrazoeugenol*), prepared from the *o*-diazotoluene chloride and sodium eugenoxide (compare Abstr., 1905, i, 492), crystallises from alcohol in dark red, prismatic needles, melts at 92—93°, and gives an *acetyl* derivative,



which crystallises from light petroleum in small, lustrous needles, melts at 72—73°, and is reduced by tin and hydrochloric acid to amino-eugenol.

*m-Toluenazoeugenol* forms small, dark red plates, and melts at 79—80°; the *acetyl* derivative forms orange-red needles and melts at 81°; *m-toluenazoeugenol ethyl ether* was obtained only as an oil.

*p-Toluenazoeugenol* forms rosettes of dark red needles, melts at 102—103°, and gives an *acetyl* derivative which crystallises in carmine needles and melts at 110—112°; *p-toluenazoeugenol ethyl ether* crystallises from dilute alcohol in red prisms or pyramids and melts at 55°.

*as-m-Xylenazoeugenol*, prepared from diazotised *as-m*-xylidine, forms red needles and melts at 108°; the *acetyl* derivative forms orange-red needles and melts at 104—105°.

*p-Xylenazoeugenol*, prepared from *p*-xylidine, forms reddish-brown crystals and melts at 97°; the *acetyl* derivative melts at 88°.

*o-Nitrobenzenazoeugenol*, prepared from diazotised *o*-nitroaniline, crystallises in lustrous, brown spangles or needles, melts at 143°, and gives an *acetyl* derivative which forms dark red needles and melts at 124°; *o-nitrobenzenazoeugenol ethyl ether* forms orange-red plates and melts at 72—73°. *m-Nitrobenzenazoeugenol* crystallises from alcohol in needles, melts at 106—107°, and gives an *acetyl* derivative which forms orange-red crystals and melts at 112°; the *ethyl ether* crystallises from alcohol in reddish-orange scales and melts at 86°.

*m-Bromobenzenazoeugenol* (*loc. cit.*) melts at 100°, not at 96°, as previously stated; its *ethyl ether* crystallises from alcohol in flattened, orange-red prisms and melts at 100—101°. *p-Chlorobenzenazoeugenol*

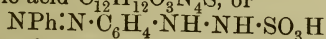
forms rusty-red needles, melts at  $117^{\circ}$ , and gives an *acetyl* derivative which crystallises in reddish-yellow needles and melts at  $113^{\circ}$ . *p*-Chlorobenzeneazoeugenol ethyl ether crystallises in silky, reddish-yellow needles and melts at  $65^{\circ}$ . *p*-Bromobenzeneazoeugenol forms dark-red prisms and melts at  $123$ — $124^{\circ}$ ; the *acetyl* derivative forms orange prisms and melts at  $123^{\circ}$ . 2:4-Dichlorobenzeneazoeugenol, prepared from 2:4-dichloroaniline, forms rust-coloured crystals and melts at  $130^{\circ}$ ; the *acetyl* derivative forms reddish-brown needles and melts at  $156^{\circ}$ .

W. A. D.

**Action of Sulphurous Acid on Diazo-*m*-toluene Chloride and Sulphate.** JULIUS TRÖGER and F. SCHAUB (*Arch. Pharm.*, 1906, 244, 302—307. Compare this vol., i, 120).—In order to obtain the sulphonic acid,  $C_{14}H_{16}O_3N_4S$ , or  $C_6H_4Me \cdot N:N \cdot C_6H_3Me \cdot NH \cdot NH \cdot SO_3H$ , in the pure state, the crude acid resulting from the action of sulphur dioxide on an aqueous diazo-*m*-toluene salt should be extracted with boiling water and then dried in a vacuum until constant in weight. Yellow to brown potassium, sodium, ammonium, *aniline*, *p*-toluidine, and *p*-xylydine salts were prepared by adding the acid to concentrated solutions of the acetates of the bases, adding so much water in the first three cases, or alcohol in the last three, that the precipitate dissolves on heating, filtering the solution, and allowing it to crystallise; the last three salts melt and decompose at  $151$ — $152^{\circ}$ ,  $154^{\circ}$ , and  $165^{\circ}$  respectively.

C. F. B.

**Action of Sulphurous Acid on Diazobenzene Sulphate.** JULIUS TRÖGER and M. FRANKE (*Arch. Pharm.*, 1906, 244, 307—312. Compare this vol., i, 120).—In presence of a large amount of sulphuric acid a diazo-sulphite is formed; when relatively less sulphuric acid is present, the sulphonic acid  $C_{12}H_{12}O_3N_4S$ , or

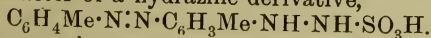


is the product; in the presence of still more water, sulphazide,  $NHPh \cdot NH \cdot SO_2Ph$ , is produced.

The crude sulphonic acid was obtained by diazotising a solution of 15 grams of aniline in 300—500 grams of water and 50 grams of concentrated sulphuric acid, and passing sulphur dioxide into the diazo-solution, kept well cooled. It was purified by adding it to a solution of ammonium acetate, diluting with so much water that the precipitate dissolved on heating, filtering the solution while hot, acidifying with dilute sulphuric acid, and allowing it to cool. The yellow to brown ammonium, *aniline*, *p*-toluidine, and *p*-xylydine salts were prepared in the way described in the preceding abstract; the last three melt and decompose at about  $165^{\circ}$ ,  $172^{\circ}$ , and  $177^{\circ}$  respectively.

C. F. B.

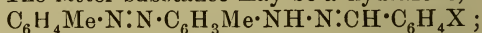
**Probable Constitutional Formula of the Sulphonic Acid,  $C_{14}H_{16}O_3N_4S$ , formed by the Action of  $SO_2$  on Diazo-*m*-toluene.** JULIUS TRÖGER, G. WARNECKE, and F. SCHAUB (*Arch. Pharm.*, 1906, 244, 312—325. Compare this vol. i, 120, and preceding abstracts).—The acid has the character of a hydrazine derivative,



Ammoniacal silver and copper solutions convert it, and mercuric oxide

converts its potassium salt, into the *silver*, *ammonium*, and *potassium* salts respectively of an *acid* containing two atoms of hydrogen less in the molecule,  $C_6H_4Me \cdot N:N \cdot C_6H_3Me \cdot N:N \cdot SO_3H$ ; this acid was only obtained as a syrup, which was converted into the *sodium* salt.

When the first sulphonic acid is treated with an aromatic aldehyde,  $C_6H_4X \cdot CHO$ , in glacial acetic acid, or in alcohol containing a little sulphuric or acetic acid, the sulphonic group is eliminated and a blue or green *sulphate* is obtained, from which ammonia liberates a red or brown *base*. The latter substance may be a hydrazone,

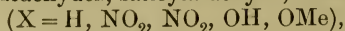


or it may have been produced by the condensation of two molecules of the hydrazine with one of the aldehyde  $(C_{14}H_{15}N_4)_2CH \cdot C_6H_4X$ , as in the case of salicylaldehyde already described. The investigation of these substances is difficult; both of them may be formed at the same time, and the conditions favouring the formation of each have not yet been ascertained. Benzaldehyde and salicylaldehyde, ( $X = H, OH$ ), form both a *hydrazone*, melting in the former case at  $159-160^\circ$ , and a tri-molecular condensation *product*, melting in the latter case at  $130^\circ$ ; *m*- and *p*-nitrobenzaldehydes, ( $X = NO_2$ ) form only *hydrazones*, which melt at  $177^\circ$  and  $160-161^\circ$  respectively; and cinnamaldehyde, forms only a tetramolecular condensation *product* melting at  $124^\circ$ . *m*-Bromobenzaldehyde yields a *base* melting at  $137^\circ$  of which the constitution has not yet been elucidated.

C. F. B.

**Probable Constitutional Formula of the Sulphonic Acid,  $C_{12}H_{12}O_3N_4S$ , formed by the Action of  $SO_2$  on a Diazobenzene Salt.** JULIUS TRÖGER, H. BERLIN, and M. FRANKE (*Arch. Pharm.*, 1906, 244, 326—335. Compare this vol., i, 120, and the preceding abstracts).—The acid has the character of a hydrazine derivative,  $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot NH \cdot NH \cdot SO_3H$ . Ammoniacal silver and copper solutions convert it respectively into the *silver* and *ammonium* salts of an acid containing two atoms of hydrogen less in the molecule,  $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot N:N \cdot SO_3H$ .

The first acid condenses, when suspended in glacial acetic acid and treated with aromatic aldehydes,  $C_6H_4X \cdot CHO$ , to yellow or red *hydrazones*,  $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot NH \cdot N:CH \cdot C_6H_4X$ ; these have the character of mono-acid bases, and unite with the sulphuric acid (produced by the elimination of the sulphonic group) to form a blue or green *sulphate*, which is decomposed more or less by hot water, completely by ammonia. No products were obtained that proceeded from the condensation of two molecules of the hydrazinesulphonic acid with one of the aldehyde. Hydrazones were obtained with benzaldehyde, *m*- and *p*-nitrobenzaldehydes, salicylaldehyde, anisaldehyde,



and cinnamaldehyde; they melt at  $168.5-169^\circ$ ,  $198-199^\circ$ ,  $173^\circ$ ,  $206^\circ$ ,  $132^\circ$ , and  $167^\circ$  respectively.

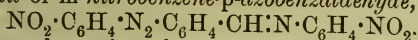
C. F. B.

**Condensation of the Three Nitroanilines with *p*-Nitrosobenzaldehyde.** FREDERICK J. ALWAY and ROSS A. GORTNER (*Amer. Chem. J.*, 1906, 38, 510—515).—The ease with which the nitroanilines condense with *p*-nitrosobenzaldehyde varies with their basicity; thus, *m*-nitro-



aniline condenses readily, *p*-nitroaniline less readily, and *o*-nitroaniline so feebly that the condensation product could not be isolated.

The *m*-nitroanil of *m*-nitrobenzene-*p*-azobenzaldehyde,

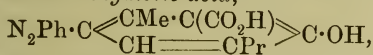


obtained by the condensation of *m*-nitroaniline with *m*-nitrosobenzaldehyde, forms brick-red, granular masses, melts at 239.5° (corr.), is readily soluble in nitrobenzene and sparingly so in alcohol or glacial acetic acid, and by prolonged treatment with hot, dilute hydrochloric acid is resolved into *m*-nitrobenzene-*p*-azobenzaldehyde and *m*-nitroaniline. *m*-Nitrobenzene-*p*-azobenzaldehyde crystallises in minute, red needles, melts at 135° (corr.) and is very soluble in alcohol, glacial acetic acid, or nitrobenzene; the substance previously described under this name (Abstr., 1904, i, 953) contained a large proportion of the *m*-nitroanil. The phenylhydrazone of *m*-nitrobenzene-*p*-azobenzaldehyde crystallises in dark red, rectangular plates and melts at 213.5° (corr.). The oxime separates from dilute alcohol in yellow crystals and melts at 116° (corr.). The anil forms small yellow crystals, and melts at 132° (corr.).

The *p*-nitroanil of *p*-nitrobenzene-*p*-azobenzaldehyde crystallises in small red needles, melts at 237—238.5° (corr.), and is sparingly soluble in alcohol but readily so in hot acetic acid. *p*-Nitrobenzene-*p*-azobenzaldehyde crystallises in long, red plates, melts at 221—222° (corr.), and is very soluble in hot benzene, glacial acetic acid, nitrobenzene, or amyl alcohol. The anil forms stellate groups of orange-coloured needles, melts at 152° (corr.), and is insoluble in alcohol. The oxime is a yellow solid which does not melt below 290°.

E. G.

**Reduction of Azo-derivatives of Aromatic Hydroxy-acids by Phenylhydrazine.** ERNESTO PUXEDDU (*Gazzetta*, 1906, 36, ii, 305—313).—*Benzeneazo-o-thymotic acid*,



prepared by the action of diazobenzene sulphate on *o*-thymotic acid dissolved in sodium hydroxide solution, crystallises from alcohol or benzene in orange-yellow, prismatic needles melting at 185—195°, and dissolves in the more common organic solvents. It gives an intensely reddish-brown coloration with ferric chloride, dissolves in concentrated sulphuric acid to a cherry-red, in concentrated hydrochloric acid to a straw-yellow liquid, and in alkali solutions to a blood-red liquid. When it is reduced by means of phenylhydrazine, the N<sub>2</sub>Ph group is doubtless replaced by NH<sub>2</sub>, but the compound thus formed loses carbon dioxide, giving the corresponding aminothymol melting at 178°.

The reduction of benzeneazo-*m*-hydroxybenzoic acid by means of phenylhydrazine proceeds with explosive violence, and yields 6-amino-3-hydroxybenzoic acid.

*o*-Tolueneazo-*m*-hydroxybenzoic acid, C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>N<sub>2</sub>, crystallises from alcohol in yellow, prismatic needles melting at 240°, and dissolves readily in the more common organic solvents. It is completely insoluble in dilute acids, but dissolves in concentrated acids, giving, with nitric acid, a deep red colour, disappearing on heating, and with sulphuric acid an intense blackish-brown liquid. Reduction with phenylhydrazine yields 6-amino-3-hydroxybenzoic acid.

*p*-Tolueneazo-*m*-hydroxybenzoic acid,  $C_{14}H_{12}O_3N_2$ , crystallises from alcohol or a mixture of alcohol and benzene in shining, prismatic needles, and melts and decomposes at  $233^\circ$ . It dissolves in organic solvents, in dilute alkali solutions, and in concentrated acids, being reprecipitated from the last-named by addition of water. Its reduction by means of phenylhydrazine proceeds explosively, and yields 6-amino-3-hydroxybenzoic acid.

*m*-Chlorobenzeneazo-*m*-hydroxybenzoic acid,  $C_{13}H_9O_3N_2Cl$ , crystallises from alcohol in orange-red, prismatic needles melting at  $225-227^\circ$ , and is soluble in concentrated acids, dilute alkali solutions, or organic solvents. Its reduction with phenylhydrazine takes place with explosive violence and yields 6-amino-3-hydroxybenzoic acid.

*p*-Chlorobenzeneazo-*m*-hydroxybenzoic acid crystallises from alcohol in orange-yellow, prismatic needles melting and decomposing at  $235-236^\circ$  and is soluble in organic solvents, concentrated acids, or dilute alkali solutions. When reduced with phenylhydrazine, it gives 6-amino-3-hydroxybenzoic acid.

T. H. P.

**The Oxidation of Benzidine.** RICHARD WILLSTÄTTER and LUDWIG KALB (*Ber.*, 1906, 39, 3474—3482).—This investigation was undertaken with the object of ascertaining the nature of a yellow, crystalline oxidation product of benzidine, obtained by oxidising the diamine with silver oxide or lead peroxide in inert solvents. This object has been attained by preparing the substance synthetically from 4-nitro-4'-aminodiphenyl, the *acetyl* derivative of which crystallises in prisms and melts at  $240^\circ$ .

4 : 4'-Diamino-4' : 4'-azodiphenyl,  $N_2(C_6H_4 \cdot C_6H_4 \cdot NH_2)_2$ , obtained by reducing 4-nitro-4'-aminodiphenyl with zinc dust and alcoholic sodium hydroxide, corresponds in every respect with the product of the oxidation of benzidine (*Abstr.*, 1905, i, 361); it crystallises in microscopic, yellowish-red needles, melts at  $287^\circ$ , and develops a characteristic blood-red coloration with concentrated sulphuric acid. The salts of this base with the mineral acids are insoluble in water; the *mono-hydrochloride*,  $C_{24}H_{20}N_4 \cdot HCl$ , consists of small, brown prisms; the *dihydrochloride*,  $C_{24}H_{20}N_4 \cdot 2HCl$ , is amorphous.

*s*-Diacetyl-4 : 4'-diamino-4' : 4'-azodiphenyl, produced from the diamine by the action of acetic anhydride, melts indefinitely and decomposes at  $373^\circ$ .

*Tetra-azo-azodiphenyl chloride*,  $N_2(C_6H_4 \cdot C_6H_4 \cdot N_2Cl)_2 \cdot 2H_2O$ , is produced most readily by diazotising the corresponding diamine with a large excess of hydrochloric acid (1 per cent.) and aqueous sodium nitrite (10 per cent.), when the salt is precipitated from the clear solution thus obtained by the addition of concentrated hydrochloric acid. The chloride, which consists of prismatic crystals having a violet reflex, gives an orange-red streak; it is moderately stable in air, and decomposes violently at about  $95^\circ$ . The tetra-azo sulphate and nitrate are both crystalline, the latter being exceptionally insoluble; the *platinichloride*,  $C_{24}H_{16}N_6PtCl_6 \cdot H_2O$ , is an insoluble, yellow, flocculent precipitate.

G. T. M.

**Action of Diazo-compounds on  $\alpha$ -Hydroxynaphthoic Acids.**

EUGÈNE GRANDMOUGIN (*Ber.*, 1906, 39, 3609—3611. Compare Nietzki and Guitermann, *Abstr.*, 1887, 732; Reverdin and De la Harpe, *Abstr.*, 1893, i, 478).—The action of diazobenzene chloride on 1-hydroxy-2-naphthoic acid in alkaline solution, leads to the formation of dibenzeneazo- $\alpha$ -naphthol (Noelting and Grandmougin, *Abstr.*, 1891, 1076), which is formed also by the action of diazobenzene chloride on benzeneazo-1-hydroxy-2-naphthoic acid.

The reduction of benzeneazo-1-hydroxy-2-naphthoic acid by means of sodium hyposulphite in aqueous alcoholic solution (compare this vol., i, 716) leads to the formation of aniline and 4-amino-1-hydroxy-2-naphthoic acid (Nietzki and Guitermann, *loc. cit.*), which crystallises in slender, colourless needles, forms a crystalline *hydrochloride*, and yields 4-amino- $\alpha$ -naphthol when heated in a current of hydrogen chloride, or naphthaquinone when treated with nitrous acid. Aniline and 3 : 4-diamino- $\alpha$ -naphthol are obtained by reduction of dibenzeneazo- $\alpha$ -naphthol by means of sodium hyposulphite.

G. Y.

**Quinoneazines.** By RICHARD WILLSTÄTTER and MAX BENZ (*Ber.*, 1906, 39, 3482—3491).—4 : 4'-Dihydroxydiphenyl and 4 : 4'-dihydroxystilbene resemble catechol in being oxidised to quinonoid substances by silver oxide or lead peroxide, but 4 : 4'-dihydroxydiphenylmethane does not exhibit this behaviour. Hence it appears that the ethylene linking  $\cdot\text{CH}:\text{CH}\cdot$  does not sever completely the quinonoid relationship between the two benzene nuclei, whereas this connexion is quite annulled by the interposition of the methylene group. It is now shown that the azo-group is analogous to the ethylene group, the *p*-azophenols undergoing the characteristic oxidation.

*p*-Benzoquinoneazine,  $\text{O}:\text{C}_6\text{H}_4:\text{N}:\text{N}:\text{C}_6\text{H}_4:\text{O}$ , prepared by shaking an ethereal solution of *p*-azophenol with silver oxide and fused sodium sulphate, crystallises from organic solvents either in dark orange-red prisms or needles or in dark yellow, rhombohedral leaflets or plates; both modifications have a blue reflex. When treated in dry ethereal solution with concentrated sulphuric acid the quinoneazine yields *p*-azophenol and an easily decomposable base; sulphurous acid or preferably phenylhydrazine reduces the quinoneazine to an azophenol which is not identical with ordinary *p*-azophenol.

The *quinhydrone*,  $\text{C}_{24}\text{H}_{18}\text{O}_4\text{N}_4$ , of *p*-benzoquinoneazine separates in bluish-black needles with a bronze reflex on mixing ethereal solutions of *p*-azophenol and the quinoneazine; it melts at 181—182° and undergoes dissociation in alcoholic solution.

4 : 4'-Dihydroxystilbene when oxidised with lead peroxide or potassium ferricyanide gives rise to stilbenequinone, which is again reduced by phenylhydrazine to the original dihydroxy-compound.

*p*-Acetylaminodiazoaminobenzene,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , the intermediate product of the interaction of diazoacetanilide and aniline, crystallises in orange-yellow, acicular prisms and melts and decomposes at 150—152°.

*p*-Aminodiazoaminobenzene,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , obtained by hydrolysing the foregoing compound with sodium ethoxide, crystallises



from dilute alcohol in brownish-yellow needles decomposing at  $157^{\circ}$ . Azoaniline, which is produced together with a preponderating amount of aminoazobenzene by warming the foregoing diazoamine with aniline and aniline hydrochloride, does not undergo the quinonoid oxidation on treatment with silver oxide or lead peroxide. G. T. M.

**Ash-free Egg Albumin.** R. W. ROSENKRANTZ (*J. Russ. Phys. Chem. Soc.*, 1906, 38, i, 2—3).—Crystals of egg-albumin obtained by a modification of the Hofmeister-Krieger process, are crystallised 6 to 10 times. They are then dissolved, dialysed, evaporated in a vacuum and again dialysed. Preparations so obtained give no ash on ignition, and do not contain recognisable quantities of ammonium sulphate. Z. K.

**Complexes of Pure Albumin.** ANDRÉ MAYER (*Compt. rend.*, 1906, 143, 515—516).—Pure ovalbumin, obtained from white of egg by diluting with water, filtering the precipitated globulins, recovering the albumin by prolonged dialysis, and repeating the processes several times, has a specific electrolytic conductivity of  $1 \cdot 10^{-5}$ , is not coagulated by heat, but forms soluble complexes with acids, (HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ), bases (NaOH, KOH), or salts [ $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ]. The amount of electrolyte absorbed by a definite quantity of ovalbumin, to raise the electrolytic conductivity from  $1 \cdot 10^{-5}$  to  $1 \cdot 10^{-4}$  varies with the nature of the electrolyte, being greater in the case of the acids than the bases or univalent salts, and greater in the case of the univalent than the bivalent salts. Ovalbumin forms insoluble complexes with salts of the heavy metals or positive colloids, which are soluble in dilute solutions of electrolytes and for this purpose  $N/160$ , HCl;  $N/140$ , NaOH; or  $N/30$ , NaCl are equivalent; from the solution a precipitate is formed by dilution or by dialysis, and the solution is coagulated by heating, the temperature at which coagulation occurs varying with the nature of the electrolyte used as the solvent. Thus a solution of an albumin-zinc salt coagulated at  $56^{\circ}$ ,  $60^{\circ}$ , or  $86^{\circ}$ , according as it had been dissolved in hydrochloric acid, sodium chloride, or potassium hydroxide respectively. In respect of all these properties, the insoluble albumin complexes closely resemble the globulins, which may be regarded as complexes of pure albumin. M. A. W.

**Distinction between Serum-albumin and Myo-albumin.** JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1906, [iii], 35, 1030—1031. Compare Abstr., 1904, i, 837; 1905, i, 728).—Aqueous extracts of the muscle of the cow, calf, horse, or turkey, and of whiting, evolve hydrogen sulphide on addition of sulphur, and this property is also exhibited by the coagulated albumins obtained by heating these extracts. The insoluble white residue, left after repeatedly washing horse-muscle with water, is almost inactive towards sulphur, and appears to behave as an inactive reserve for the more active and soluble myo-albumin. The latter is rendered inactive by contact with sulphur for several days, and the coagulum obtained from this is similarly inactive towards sulphur. An analogous non-philothionic myo-albumin may be obtained by extracting the uterus of

the sheep with dilute alcohol; the fresh tissue furnishes traces of hydrogen sulphide with sulphur, but the coagulum obtained by heating the alcoholic extract gives none.

T. A. H.

**Philothionic Hydrogen.** JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1906, [iii], 35, 1031—1033. Compare preceding abstract and Heffter and Hausmann, *Abstr.*, 1904, i, 461).—The philothionic hydrogen of myo-albumin is not destroyed after 15 days' exposure to air at the atmospheric temperature, whereas it is much more rapidly removed by sulphur (see preceding abstract). In this connexion it is pointed out that hydrogen and sulphur combine at 250°, whereas hydrogen and oxygen do not unite below 350°, and it is suggested that whilst philothion seems to be capable of effecting the same chemical change as is induced by an increase in temperature of about 250°, its activity is insufficient to cause a combination which requires an increase of 350°.

T. A. H.

**Monoamino-acids of the Crystalline Proteid from Pumpkin Seeds.** EMIL ABDERHALDEN and OSCAR BERGHAUSEN (*Zeit. physiol. Chem.*, 1906, 49, 15—20).—The substances obtained from the cleavage of edestin (vitellin) by means of dilute sulphuric acid were: glycine, 0·08; alanine, present; aminovaleric acid, 0·7; leucine, 4·7; proline, 1·7; glutamic acid, 13·4; aspartic acid, 4·5; phenylalanine, 2·6; and tyrosine, 1·4 per cent.

W. D. H.

**Optical Rotation of Gliadin in Certain Organic Solvents.** W. E. MATHEWSON (*J. Amer. Chem. Soc.*, 1906, 28, 1482—1485. Compare this vol., i, 545).—The specific rotatory powers of solutions of gliadin in methyl, ethyl, propyl, and benzyl alcohols, phenol, *p*-cresol, and glacial acetic acid have been determined, and the results are tabulated. The gliadin was prepared from wheat-flour, and the experiments were made in connexion with an investigation which is in progress with a view to the improvement of the methods of flour analysis.

E. G.

**Iodospongine. Preliminary Note.** L. SCOTT (*Chem. Centr.*, 1906, ii, 1133; from *Biochem. Zeit.*, 1906, 1, 367).—The non-digestible residue of sponge substance can be rendered soluble by treatment with concentrated sulphuric acid. The product is then digested with pancreatic juice until it no longer gives the biuret reaction. After separating the diamino-acids, an organic compound, rich in iodine, is obtained, which is purified from monoamino-acids by the fractional crystallisation of its copper salt.

P. H.

**The Rendering Insoluble of Gelatin by Formaldehyde.** AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 872—879. Compare this vol., i, 614, 915).—When gelatin is soaked in a solution of formaldehyde, the insoluble product formed contains from 4 to 4·8 per cent. of the aldehyde. The rapidity with which the formaldehyde is absorbed under these conditions increases with the concentration of the solution, but is not

sensibly influenced by increase of temperature. Gaseous formaldehyde is absorbed more slowly by gelatin, but the product ultimately formed is similar to that obtained in the first case. The precipitate produced by mixing solutions of gelatin and formaldehyde contains unaltered gelatin.

Gelatin rendered insoluble by formaldehyde is slowly decomposed by hot water, and the formaldehyde may be completely eliminated by this means. The same decomposition is brought about by macerating the product in cold, dilute hydrochloric acid, and this method was used for the liberation and ultimate estimation of the formaldehyde by Seyewetz and Gibello's process (*Abstr.*, 1904, ii, 521). The formaldehyde is also gradually liberated from the insoluble product when the latter is heated at 110°. From these results it is concluded that when gelatin is treated with formaldehyde, an additive product rather than a true compound is formed. T. A. H.

**Intramolecular Absorption of Water in the Tryptic Digestion of Proteid.** PAUL HÁRI (*Pflüger's Archiv*, 1906, 115, 52—63).—Elementary analysis shows that the products (peptone) of the action of trypsin on proteids contain more oxygen and more hydrogen than the original material. This is attributed to the intramolecular absorption of water. W. D. H.

**Tryptophan.** CARL NEUBERG (*Chem. Centr.*, 1906, ii, 892; from *Charité Ann.*, 30).—The author suggests the following modification of Hopkins and Cole's method of preparing tryptophan. In the second precipitation with mercuric sulphate the first portions, consisting almost entirely of cystine and mercury-cysteine, should be rejected; the filtrate is then treated with hydrogen sulphide, and after boiling off the excess of the latter, an excess of lead carbonate is added (100 grams of lead carbonate per kilogram of casein). The whole is then warmed on a water-bath for half an hour, ammonia is added until the solution smells faintly, and the heating is continued for a quarter of an hour more. The dissolved lead is then precipitated by means of hydrogen sulphide and the solution is evaporated; perfectly pure, white tryptophan separates out in a yield of 7—8 grams per kilogram of well-digested casein. P. H.

**Myelin Bodies.** J. G. ADAMI and L. ASCHOFF (*Proc. Roy. Soc.*, 1906, 78 B, 359—368).—The term myelin was originally applied by Virchow to a constituent of the white substance of nerves which swells up with water, and develops curious forms with a double contour. Myelin bodies have since then been described in many situations in cell protoplasm under both physiological and pathological conditions. Many soaps exhibit the same phenomena. The globules formed are doubly refracting, and the hypothesis is advanced that they are fluid sphaerocrystals. With regard to their chemical composition there is still much doubt, but the evidence appears to point to two principal varieties, namely, cholesterol oleate and choline oleate. W. D. H.



REPORT OF  
THE INTERNATIONAL COMMITTEE  
ON ATOMIC WEIGHTS.

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THE Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

GOVERNMENT LABORATORY,  
CLEMENT'S INN PASSAGE,  
STRAND, LONDON, W.C.  
15th November, 1906.

GENTLEMEN,

I have the honour to forward to you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1907, to which I have affixed, as desired by them, the names of Professors Moissan and Ostwald.

The Committee, for reasons stated in the Report, have suggested new values for the atomic weights of bismuth, nitrogen, tantalum, and terbium, and they are further of opinion that alterations are needed in the atomic weights of silver and chlorine, but before recommending any change as regards these elements they consider it expedient to wait for fuller information of the results of determinations known to be in progress. The new values for silver and chlorine will, of course, have an influence upon a large number of atomic weights.

I am, Gentlemen,  
Your obedient Servant,  
T. E. THORPE.

*The Hon. Secretaries,  
The Chemical Society,  
Burlington House,  
London, W.*

Report of the International Committee on Atomic Weights, 1907.

Since the preparation of our last report, for 1906, a number of important memoirs upon atomic weights have appeared. The results obtained may be briefly summarised as follows:

*Bismuth.*—Work done at Erlangen under the direction of Gutbier (*Zeit. Elektrochem.*, 1905, 11, 831) has been published in the form of three doctoral dissertations (L. Birckenbach, 1905; H. Mehler, 1905; R. L. Janssen, 1906). Birckenbach, by synthesis of the oxide from the metal, found, in mean,  $\text{Bi} = 208.05$ . A series of reductions of the oxide gave  $\text{Bi} = 208.08$ . Mehler determined the ratio  $\text{BiBr}_3 : \text{AgBr}$ , and found  $\text{Bi} = 208.05$ . By synthesis of the sulphate from the metal, Janssen obtained the value  $\text{Bi} = 208.074$ . These determinations are concordant, and also agree with the earlier measurements by Schneider and Löwe and with a series by Marignac. The atomic weight of bismuth, therefore, is to be taken as 208.0 in round numbers, and the value 208.5, as hitherto given in our table, is too high.

*Bromine.*—Baxter's (*J. Amer. Chem. Soc.*, 1906, 28, 1322) determinations of this constant are based upon the antecedent values  $\text{Ag} = 107.93$  and  $\text{Cl} = 35.473$ . Eighteen syntheses of silver bromide gave, in mean,  $\text{Br} = 79.953$ . Thirteen experiments upon the conversion of  $\text{AgBr}$  into  $\text{AgCl}$  gave  $\text{Br} = 79.952$ .

*Cadmium.*—The memoir by Baxter, Hines, and Frevert (*ibid.*, 1906, 28, 770) is a continuation of the research which was noted last year. Four ratios were measured with the following results, when  $\text{Ag} = 107.93$ :

$\text{CdBr}_2 : 2\text{Ag}$ .	$\text{Cd} = 112.470$ .
$\text{CdBr}_2 : 2\text{AgBr}$ .	$\text{Cd} = 112.464$ .
$\text{CdCl}_2 : 2\text{Ag}$ .	$\text{Cd} = 112.471$ .
$\text{CdCl}_2 : 2\text{AgCl}$ .	$\text{Cd} = 112.470$ .

*Copper.*—A series of analyses and syntheses of copper oxide by Murmann (*Monatsh.*, 1906, 27, 351) gave the value  $\text{Cu} = 63.53$ . The data are not concordant, and the determinations are not entitled to much weight.

*Iodine.*—Gallo (*Gazzetta*, 1906, 36, 116) has determined the atomic weight of iodine electrolytically, comparing the iodine liberated by a current with the silver deposited. His values range from 126.82 to 126.98, or, in mean, 126.89 when  $\text{Ag} = 107.93$ . This result is more nearly in accord with the determination by Stas than with the later measurements.

*Nitrogen.*—Gray's (*Trans.*, 1905, 87, 1601) work upon the atomic weight of this element, noticed in our report for 1906, has since been published in full. His mean results are as follows: from the density of nitric oxide,  $\text{N} = 14.006$ ; from the analysis of nitric oxide,  $\text{N} = 14.010$ ; from the density of nitrogen,  $\text{N} = 14.008$ . The mean of all the determinations is  $\text{N} = 14.0085$ , or very nearly 14.01. This agrees closely with the earlier measurements by Guye, Rayleigh, and Leduc, and leaves no reasonable doubt but that the new value should

replace the 14.04 as given in our annual table. In a later paper (*Trans.*, 1906, 89, 1173) Gray has gathered corroborative evidence from various sources, and has discussed Stas's ratios in order to discover their possible errors. Other discussions of similar purport are by Guye \* and Scott (*Chem. News*, 1906, 93, 20), but they are not final. Experimental evidence alone can reveal the cause of discrepancy between the new figure and the old.

**Palladium.**—Amberg (*Annalen*, 1905, 341, 235) has redetermined the atomic weight of palladium by analysis of palladosoammine chloride,  $\text{PdN}_2\text{H}_6\text{Cl}_2$ . The value obtained is  $\text{Pd} = 106.688$ , or 106.7 nearly. Five other analyses of the same salt, by Krell (*Inaug. Dissertation*, Erlangen, 1906), gave a mean of  $\text{Pd} = 106.694$ . Recalculated with Richards's value for Cl, and rejecting one experiment as defective, Krell concludes that  $\text{Pd} = 106.78$ , but this again would be lowered by the adoption of the newer value for N. Any change in this constant may well be deferred until the antecedent atomic weights are more definitely known.

**Silver.**—In an attempt to determine the source of error in Stas's figures for nitrogen, Guye and Ter Gazarian† examined the fundamental potassium chlorate ratio. They found that potassium chlorate crystallises with a small quantity of chloride as an impurity, the amount being nearly constant and about 2.7 parts in ten thousand. Applying this correction to Stas's ratios, his value for silver is lowered from 107.93 to 107.89. A re-discussion of ten fundamental ratios gave figures for silver ranging from 107.871 to 107.908, or 107.89 in mean. If this conclusion is sustained, the Stas's ratios for silver nitrate will give a value for nitrogen in harmony with the figures obtained by Guye and Gray.

**Tantalum.**—Hinrichsen and Sahlbom (*Ber.*, 1906, 39, 2600) have determined the atomic weight of tantalum by conversion of the metal into the pentoxide. Five such syntheses gave  $\text{Ta} = 180.59$  to 181.77, or 181.0 in mean. This value should replace the old determination by Marignac as given in our previous tables.

**The Rare Earths.**—On the metals of this group a notable amount of work has been published during 1906. From five determinations of water in terbium sulphate, Urbain (*Compt. rend.*, 1906, 142, 957) deduces the value  $\text{Tb} = 159.22$ ; and this should supplant the older, questionable data. In another paper (*ibid.*, 1906, 142, 785) Urbain gives an atomic weight of 163.49 to dysprosium, but without details or weighings.

\* *Ber.*, 1906, 39, 1470. For Guye and Bogdan's complete memoir upon nitrous oxide, see *J. Chim. phys.*, 1905, 3, 537.

† *Compt. rend.*, 1906, 143, 411. See also *J. Chim. phys.*, 1906, 4, 174, for a paper by Guye on the need of a general recalculation of atomic weights.



By a volumetric method, Feit and Przibylla (*Zeit. anorg. Chem.*, 1906, 50, 249) have determined the amount of sulphuric acid required to neutralise several of the oxides in this group, and have in that way obtained new estimates of the corresponding atomic weights. The final results, reduced to a vacuum standard, are as follows :

Lanthanum.....	139·17	Europium .....	152·66
Praseodymium .....	140·62	Gadolinium.....	157·38
Neodymium .....	144·52	Ytterbium .....	173·52
Samarium .....	150·47	Yttrium .....	89·40

In Abegg's *Handbuch der anorganische Chemie*, Brauner has given full summaries of all atomic weight determinations. With these summaries, in connexion with the rare earth metals (in Bd. 3, Abth. 1, pp. 263, 276, 284, 304, 318, 335), he has cited some hitherto unpublished determinations of his own. His results are :

Praseodymium .....	140·97	Gadolinium.....	155·78
Neodymium .....	143·89	Erbium .....	167·14
Samarium .....	150·71	Ytterbium .....	173·08

Among these figures that for Gd is admittedly too low, and that for Sa is vitiated by the presence of europium in the material studied.

From the evidence presented in this report, and in preceding years, we now feel justified in recommending the following changes in the table :

Nitrogen, from	14·04	to	14·01.
Bismuth, „	208·5	„	208·0.
Tantalum, „	183·0	„	181·0.
Terbium, „	160·0	„	159·2.

Other changes which seem to be needed because of alterations in the atomic weights of silver and chlorine cannot yet be made with safety. The atomic weight of silver, as deduced from Stas's data, is probably too high, but by an unknown amount, and that will affect the entire table. If we assume, with Guye, that  $\text{Ag} = 107·89$ , with the proportional changes in Cl and Br, the atomic weight of barium, as determined by Richards, will be reduced by 0·05. Such a change, which is probably extreme, does not affect the utility of the accepted atomic weights at all seriously, and no important interest will suffer if we delay the suggested alterations until our knowledge of the corrections to be applied is more exact. Guye's conclusions, although strongly supported, are not final, and they should be neither accepted nor rejected except upon the basis of much more complete evidence

than we now possess. The atomic weight of chlorine, as given in our last report, is certainly too low, but it depends in part upon the undetermined change to be applied to silver. For that reason, as well as for the reason that a change in chlorine affects many other values, we prefer to leave the figures as they are and to wait for fuller information. That information will doubtless be supplied by researches now known to be in progress, and the corrections which they will furnish ought not to be delayed very long.

One addition to the table seems to be legitimate. Europium, with an approximate atomic weight of 152, appears to be a definite element, as shown by the investigations of Demarçay, Urbain and Lacombe, Eberhard, and Feit and Przibylla. Its existence is recognised in Abegg's Handbuch, and its claims to a place in the table are certainly as great as those of erbium, thulium, or terbium. As for dysprosium, its admission to the table may well be delayed until a better determination of its atomic weight shall have been made.

In conclusion, we urge upon all chemists who are engaged in the determination of atomic weights to send copies of their publications to all the members of this committee in order that their work may be promptly recognised and not overlooked. Data published in standard journals are of course easily found, but publications of local societies and doctoral dissertations might readily escape our notice.

Professor Seubert, an original member of this committee, has resigned. Professor Ostwald has been designated as his successor.\*

The table offered for 1907 is appended hereto.

F. W. CLARKE,  
HENRI MOISSAN,  
WILHELM OSTWALD,  
T. E. THORPE.

\* See *Ber.*, 1906, 39, 2176, for the formal announcement of this change.

1907.

*International Atomic Weights.*

Aluminium .....	Al	27·1	Neodymium .....	Nd	143·6
Antimony .....	Sb	120·2	Neon .....	Ne	20
Argon .....	A	39·9	Nickel .....	Ni	58·7
Arsenic .....	As	75·0	Nitrogen .....	N	14·01
Barium .....	Ba	137·4	Osmium .....	Os	191
Bismuth .....	Bi	208·0	Oxygen .....	O	16·00
Boron .....	B	11·0	Palladium .....	Pd	106·5
Bromine .....	Br	79·96	Phosphorus .....	P	31·0
Cadmium .....	Cd	112·4	Platinum .....	Pt	194·8
Cæsium .....	Cs	132·9	Potassium .....	K	39·15
Calcium .....	Ca	40·1	Praseodymium .....	Pr	140·5
Carbon .....	C	12·00	Radium .....	Rd	225
Cerium .....	Ce	140·25	Rhodium .....	Rh	103·0
Chlorine .....	Cl	35·45	Rubidium .....	Rb	85·5
Chromium .....	Cr	52·1	Ruthenium .....	Ru	101·7
Cobalt .....	Co	59·0	Samarium .....	Sa	150·3
Columbium .....	Cb	94	Scandium .....	Sc	44·1
Copper .....	Cu	63·6	Selenium .....	Se	79·2
Erbium .....	Er	166	Silicon .....	Si	28·4
Europium .....	Eu	152	Silver .....	Ag	107·93
Fluorine .....	F	19·0	Sodium .....	Na	23·05
Gadolinium .....	Gd	156	Strontium .....	Sr	87·6
Gallium .....	Ga	70	Sulphur .....	S	32·06
Germanium .....	Ge	72·5	Tantalum .....	Ta	181
Glucinum .....	Gl	9·1	Tellurium .....	Te	127·6
Gold .....	Au	197·2	Terbium .....	Tb	159·2
Helium .....	He	4·0	Thallium .....	Tl	204·1
Hydrogen .....	H	1·008	Thorium .....	Th	232·5
Indium .....	In	115	Thulium .....	Tm	171
Iodine .....	I	126·97	Tin .....	Sn	119·0
Iridium .....	Ir	193·0	Titanium .....	Ti	48·1
Iron .....	Fe	55·9	Tungsten .....	W	184
Krypton .....	Kr	81·8	Uranium .....	U	238·5
Lanthanum .....	La	138·9	Vanadium .....	V	51·2
Lead .....	Pb	206·9	Xenon .....	Xe	128
Lithium .....	Li	7·03	Ytterbium .....	Yb	173·0
Magnesium .....	Mg	24·36	Yttrium .....	Yt	89·0
Manganese .....	Mn	55·0	Zinc .....	Zn	65·4
Mercury .....	Hg	200·0	Zirconium .....	Zr	90·6
Molybdenum .....	Mo	96·0			



# INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

## NOMENCLATURE AND SYSTEM OF NOTATION

### ADOPTED IN THE ABSTRACTS.

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THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.
2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.
3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.
4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.
5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.
6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.
7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.
8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.
9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

## Nomenclature.

10. Employ names such as *sodium chloride*, *potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

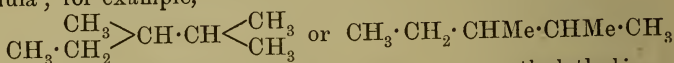
11. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulae*.

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO<sub>2</sub>, carbon dioxide; P<sub>4</sub>O<sub>10</sub>, phosphoric oxide; As<sub>4</sub>O<sub>6</sub>, arsenious oxide; Fe<sub>2</sub>O<sub>3</sub>, ferric oxide.

14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter *a* being assigned to the first carbon atom in the formula, except in the case of CN and CO<sub>2</sub>H, for example, CH<sub>3</sub>·CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>I *a*-iodobutane, CH<sub>3</sub>·CH<sub>2</sub>·CH<sub>2</sub>·CN *a*-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,



should be termed *βγ*-dimethylpentane, not *methylethylisopropylmethane*, and  $\begin{array}{c} \text{CH}_3 \\ \diagup \end{array} \text{CH} \cdot \text{CH} \begin{array}{c} \diagdown \\ \text{CH}_3 \end{array} \text{ or } \text{CH}_3 \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$  should be termed *αβ*-dimethylbutyric acid, not *αββ*-trimethylpropionic, or *α-methylisovaleric*, or *methylisopropylacetic acid*.

16. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C<sub>n</sub>H<sub>2n+2</sub> series of the form CH<sub>3</sub>·[CH<sub>2</sub>]<sub>5</sub>·CH<sub>3</sub>, &c. Term the hydrocarbons C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name *allene* for the hydrocarbon CH<sub>2</sub>:C:CH<sub>2</sub>.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocýano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus  $\alpha$ -ethoxypropionic acid,  $\text{OEt} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid,  $(\text{OEt})_2\text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H}$ , instead of diethylprotocatechuic acid; and  $\alpha$ -acetoxypropionic acid,  $\text{OAc} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus,  $\text{C}_6\text{H}(\text{Et})_2(\text{OH})_2 \cdot \text{CO}_2\text{H}$ , and not  $\text{C}_6\text{H}_3(\text{OEt})_2 \cdot \text{CO}_2\text{H}$ , just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula  $\text{C}_6\text{HBr}_2(\text{OH})_2 \cdot \text{CO}_2\text{H}$ .

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups  $\text{NH}_2$ ,  $\text{NHR}$ ,  $\text{NR}_2$ ,  $\text{NH}$  or  $\text{NR}$ , its name should end in *ino*; for example,  $\beta$ -aminopropionic acid,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ,  $\beta$ -anilino-acrylic acid,  $\text{NHPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ ,  $\alpha$ -iminopropionic acid,  $\text{NH} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$ .

22. Compounds of the radicle  $\text{SO}_3\text{H}$  should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 3rd decade (1893–1902) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

### Notation.

25. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

- (a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.



(b) That formulæ should be shortened by the judicious employment of the symbols Me for  $\text{CH}_3$ , Et for  $\text{C}_2\text{H}_5$ ,  $\text{Pr}^a$  for  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$ ,  $\text{Pr}^s$  for  $\text{CH}(\text{CH}_3)_2$ , Ph for  $\text{C}_6\text{H}_5$ , Py for  $\text{C}_5\text{H}_4\text{N}$ , Ac for  $\text{CO}\cdot\text{CH}_3$ , and Bz for  $\text{CO}\cdot\text{C}_6\text{H}_5$ .

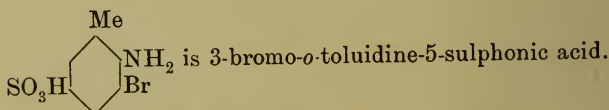
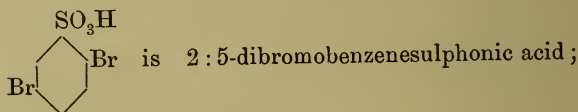
(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

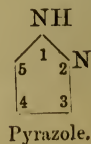
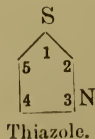
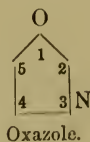
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

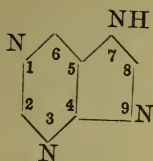
(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed ; for example :—

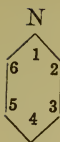


29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (2nd edition, 1899, pp. 16—26) should be used, of which the following schemes may be regarded as typical :—





Purine.\*



Pyridine.



Indole.



Naphthalene.



Quinoline.



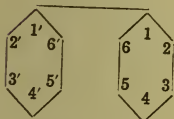
isoQuinoline.



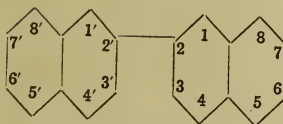
Anthracene.



Phenanthrene.



Diphenyl.

 $\beta\beta$ -Dinaphthyl.**Manuscript.**

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 x 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

**Proofs.**

34. Abstractors are expected to read and correct proofs carefully, and to check all formulæ and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

\* \* The Editor's decision, in all matters connected with the Abstracts, must be considered final.

\* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.

# JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, 34, 2455; *Bull. Soc. chim.* 1901, [iii], 25, 794; *Gazzetta* 1901, 31, i, 554.

ABBREVIATED TITLE.	JOURNAL.
<i>Amer. Chem. J.</i> . . .	American Chemical Journal.
<i>Amer. J. Pharm.</i> . . .	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i> . . .	American Journal of Physiology.
<i>Amer. J. Sci.</i> . . .	American Journal of Science.
<i>Anal. Fis. Quim.</i> . . .	Anales de la Sociedad Española Física y Química.
<i>Analyst</i> . . .	The Analyst.
<i>Annalen</i> . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Physik</i> . . .	Annalen der Physik.
<i>Ann. Chim. anal.</i> . . .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim. Phys.</i> . . .	Annales de Chimie et de Physique.
<i>Ann. Inst. Pasteur</i> . . .	Annales de l'Institut Pasteur.
<i>Ann. sci. Univ. Jassy</i> . . .	Annales scientifiques de l'Université de Jassy.
<i>Arch. expt. Path. Pharm.</i> . . .	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Hygiene</i> . . .	Archiv für Hygiene.
<i>Arch. Néerland.</i> . . .	Archives Néerlandaises des sciences exactes et naturelles.
<i>Arch. Pharm.</i> . . .	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i> . . .	Archives des Sciences physiques et naturelles.
<i>Arkiv Kem. Min. Geol.</i> . . .	Arkiv för Kemi, Mineralogi och Geologi.
<i>Atti R. Accad. Sci. Torino.</i> . . .	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i> . . .	Atti della Reale Accademia dei Lincei.
<i>Beitr. chem. Physiol. Path.</i> . . .	Beiträge für chemische Physiologie und Pathologie.
<i>Ber.</i> . . .	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i> . . .	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i> . . .	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Ber. Deut. physikal. Ges.</i> . . .	Berichte der Deutschen physikalischen Gesellschaft.
* <i>Bied. Zentr.</i> . . .	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
<i>Bio-Chem. J.</i> . . .	The Bio-Chemical Journal.
<i>Bio-chem. Zeitsch.</i> . . .	Biochemische Zeitschrift.
<i>Boll. chim. farm.</i> . . .	Bollettino chimico farmaceutico.
<i>Bull. Acad. roy. Belg.</i> . . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i> . . .	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Assoc. chim. Sucr. Dist.</i> . . .	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
<i>Bull. Coll. Agr. Tōkyō</i> . . .	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
<i>Bull. Geol. Soc. Amer.</i> . . .	Bulletin of the Geological Society of America.
<i>Bull. Imp. Inst.</i> . . .	Bulletin of the Imperial Institute.
<i>Bull. Soc. chim.</i> . . .	Bulletin de la Société chimique de Paris.
<i>Bull. Soc. chim. Belg.</i> . . .	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. franç. Min.</i> . . .	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. ind. Mulhouse</i> . . .	Bulletin de la Société industrielle de Mulhouse.
<i>Centr. Bakt. Par.</i> . . .	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
<i>Centr. Min.</i> . . .	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* <i>Chem. Zentr.</i> . . .	Chemisches Zentralblatt.

\* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.



# JOURNALS FROM WHICH ABSTRACTS ARE MADE.

## ABBREVIATED TITLE.

## JOURNAL.

<i>Chem. News</i> . . . . .	Chemical News.
<i>Chem. Rev. Fett-Harz-Ind.</i> . . . . .	Chemische Revue über die Fett- und Harz-Industrie.
<i>Chem. Weekblad</i> . . . . .	Chemisch Weekblad.
<i>Chem. Zeit.</i> . . . . .	Chemiker Zeitung.
<i>Compt. rend.</i> . . . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Exper. Stat. Record</i> . . . . .	Experiment Station Record.
<i>Gazzetta</i> . . . . .	Gazzetta chimica italiana.
<i>Geol. Mag.</i> . . . . .	Geological Magazine.
<i>Jahrb. Min.</i> . . . . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>Jahrb. Min. Beil.-Bd.</i> . . . . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
<i>Jahrb. Radioaktiv. Elektronik.</i> . . . . .	Jahrbuch der Radioaktivität und Elektronik.
<i>J. Amer. Chem. Soc.</i> . . . . .	Journal of the American Chemical Society.
<i>J. Biol. Chem.</i> . . . . .	Journal of Biological Chemistry, New York.
<i>J. Chim. phys.</i> . . . . .	Journal de Chimie physique.
<i>J. Geol.</i> . . . . .	Journal of Geology.
<i>J. Hygiene</i> . . . . .	Journal of Hygiene.
<i>J. Inst. Brewing</i> . . . . .	Journal of the Institute of Brewing.
<i>J. Landw.</i> . . . . .	Journal für Landwirtschaft.
<i>J. Med. Research</i> . . . . .	Journal of Medical Research.
<i>J. Path. Bact.</i> . . . . .	Journal of Pathology and Bacteriology.
<i>J. Pharm. Chim.</i> . . . . .	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i> . . . . .	Journal of Physical Chemistry.
<i>J. Physiol.</i> . . . . .	Journal of Physiology.
<i>J. Physique</i> . . . . .	Journal de Physique.
<i>J. pr. Chem.</i> . . . . .	Journal für praktische Chemie.
<i>J. Roy. Agric. Soc.</i> . . . . .	Journal of the Royal Agricultural Society.
<i>J. Roy. Soc. New South Wales.</i> . . . . .	Journal of the Royal Society of New South Wales.
<i>J. Russ. Phys. Chem. Soc.</i> . . . . .	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i> . . . . .	Journal of the Society of Chemical Industry.
<i>K. Svenska Vet-Akad. Handl.</i> . . . . .	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
<i>Lancet.</i> . . . . .	The Lancet.
<i>Landw. Versuchs-Stat.</i> . . . . .	Die landwirtschaftlichen Versuchs-Stationen.
<i>L'Orosi</i> . . . . .	L'Orosi.
<i>Mem. Accad. Sci. Torino</i> . . . . .	Memorie della Reale Accademia delle Scienze di Torino.
<i>Mem. Coll. Sci. Eng. Kyōtō.</i> . . . . .	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
<i>Mem. Manchester Phil. Soc.</i> . . . . .	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Metallurgie</i> . . . . .	Metallurgie.
<i>Milch. Zentr.</i> . . . . .	Milchwirtschaftliches Zentralblatt.
<i>Min. Mag.</i> . . . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i> . . . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Nuovo Cim.</i> . . . . .	Il Nuovo Cimento.
<i>Pflüger's Archiv.</i> . . . . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. Arch.</i> . . . . .	Pharmaceutical Archives.
<i>Pharm. Centr.-h.</i> . . . . .	Pharmazeutische Centralhalle.
<i>Pharm. J.</i> . . . . .	Pharmaceutical Journal.
<i>Pharm. Rev.</i> . . . . .	Pharmaceutical Review.
<i>Pharm. Weekblad</i> . . . . .	Pharmaceutisch Weekblad.
<i>Pharm. Zeit.</i> . . . . .	Pharmazeutische Zeitung.
<i>Phil. Mag.</i> . . . . .	Philosophical Magazine (The London, Edinburgh and Dublin).

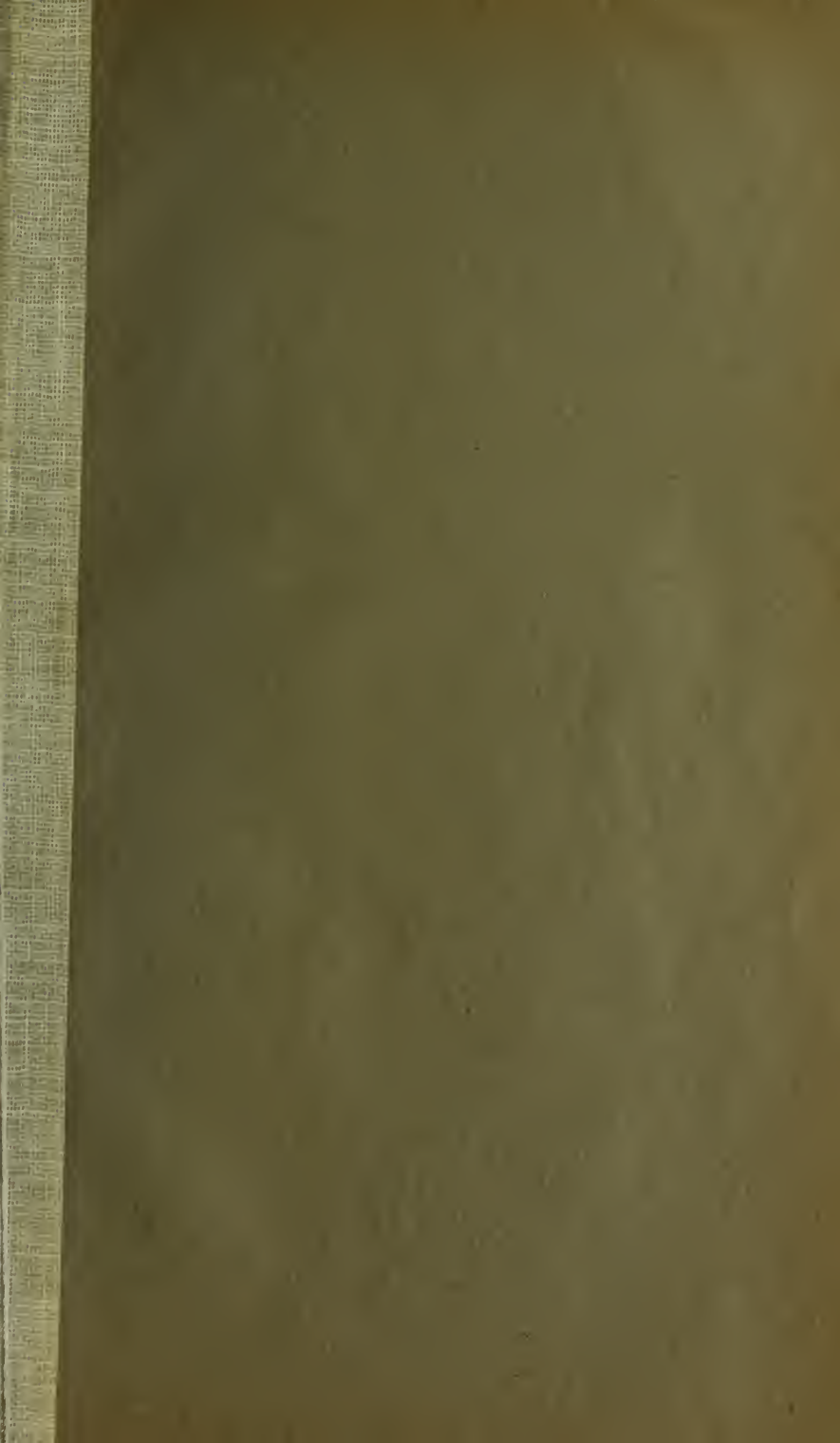
# JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Physikal. Zeitsch.</i>	Physikalische Zeitschrift.
<i>Proc. Amer. Physiol. Soc.</i>	Proceedings of the American Physiological Society.
<i>Proc. Camb. Phil. Soc.</i>	Proceedings of the Cambridge Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam.</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Phil. Soc. Glasgow</i>	Proceedings of the Glasgow Philosophical Society.
<i>Proc. Physiol. Soc.</i>	Proceedings of the Physiological Society.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i>	Proceedings of the Royal Society of Edinburgh.
<i>Quart. J. Geol. Soc.</i>	Quarterly Journal of the Geological Society.
<i>Rec. trav. chim.</i>	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rend. Accad. Sci. Fis. Mat. Napoli.</i>	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
<i>Rev. de Métallurgie</i>	Revue de Métallurgie.
<i>Rev. intern. Falsif.</i>	Revue internationale des Falsifications.
<i>Sci. Proc. Roy. Dubl. Soc.</i>	Scientific Proceedings of the Royal Dublin Society.
<i>Sci. Trans. Roy. Dubl. Soc.</i>	Scientific Transactions of the Royal Dublin Society.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i>	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. München.</i>	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
<i>Trans. Amer. Electrochem. Soc.</i>	Transactions of the American Electrochemical Society.
<i>Trans. Amer. Inst. Mining Eng.</i>	Transactions of the American Institute of Mining Engineers.
<i>Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>Trans. Nova Scotia Inst. Sci.</i>	Transactions of the Nova Scotia Institute of Science.
<i>Trans. Path. Soc.</i>	Transactions of the Pathological Society.
<i>Trans. Roy. Soc. Canada</i>	Transactions of the Royal Society of Canada.
<i>Trans. Roy. Irish Acad.</i>	Transactions of the Royal Irish Academy.
<i>Tsch. Min. Mitt.</i>	Tschermak's Mineralogische Mittheilungen.
<i>U.S.A. Dept. Agric. Bull.</i>	Bulletins of the Department of Agriculture, U.S.A.
<i>U.S.A. Dept. Agric. Rep.</i>	Reports of the Department of Agriculture, U.S.A.
<i>Verh. Ges. deut. Naturforsch. Aerzte</i>	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
<i>Wiss. Abhandl. Phys.-Tech. Reichsanstalt.</i>	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
<i>Zeitsch. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i>	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Biol.</i>	Zeitschrift für Biologie.
<i>Zeitsch. Elektrochem.</i>	Zeitschrift für Elektrochemie.
<i>Zeitsch. Farb. Ind.</i>	Zeitschrift für Farben-Industrie.
<i>Zeitsch. Kryst. Min.</i>	Zeitschrift für Krystallographie und Mineralogie.
<i>Zeitsch. Nahr. Genussm.</i>	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. öffentl. Chem.</i>	Zeitschrift für öffentliche Chemie.
<i>Zeitsch. physikal. Chem.</i>	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. prakt. Geol.</i>	Zeitschrift für praktische Geologie.
<i>Zeitsch. Ver. deut. Zuckerind.</i>	Zeitschrift des Vereins der deutschen Zucker-Industrie.
<i>Zeitsch. Zuckerind. Böhm.</i>	Zeitschrift für Zuckerindustrie in Böhmen.















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